1-1-1994

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Recommended Citation

Neill, John Thomas, "Miscibility in blends of poly(vinyl chloride) and chlorinated poly(vinyl chloride) with polycarbonates/" (1994). *Doctoral Dissertations 1896 - February 2014*. 831.
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MISCIBILITY IN BLENDS OF POLY(VINYL CHLORIDE) AND CHLORINATED POLY(VINYL CHLORIDE) WITH POLYCARBONATES

A Dissertation Presented

by

JOHN THOMAS NEILL

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 1994

Polymer Science and Engineering

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To Mickey

ACKNOWLEDGEMENTS

I would like to thank my advisor, Prof. Frank Karasz, for his helpful comments on the research, which not only enlightened me on the topic of polymer blends, but often put me back on the research track. His assistance in creating bright, colorful presentations is also greatly appreciated. I would also like to thank the members of my thesis committee, Professors William MacKnight and James Donovan.

Members of the Karasz and MacKnight research groups, past and present, deserve thanks for assistance in the operation of equipment and discussions of blend-related topics. Dave Rice and Roberto Gregorius assisted with solid-state and solution NMR measurements. Nancy, Vicky, Jennifer, Susan, Kevin, and Cary were all very helpful, doing all of the "behind the scenes" work. For financial support, I would like to thank B. F. Goodrich Company and the Air Force Office of Scientific Research.

I would like to thank Prof. Paul Lahti for time discussing polycarbonate electronic structures and calculating electron densities. I am grateful to Wei-Ming Tang and Joan Vrtis for their assistance on the Instron. Thanks also to Murali "Raj" at Goodrich for his assistance in acquiring polymer samples for study.

And last, but not least, I need to thank my personal support group: my wife, Michelle, who provided just the right amounts of patience and pushing to get me through this

research; my parents and in-law's for their tremendous support throughout the grad school years. I would like to thank all family and friends who have offered encouragement over the past four years.

ABSTRACT

MISCIBILITY IN BLENDS OF POLY(VINYL CHLORIDE) AND CHLORINATED POLY(VINYL CHLORIDE) WITH POLYCARBONATES

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Blends of aromatic polycarbonates with poly(vinyl chloride) (PVC) and chlorinated poly(vinyl chloride) (CPVC) have been investigated. The polycarbonates include homopolymers and copolymers based on bisphenol-A derivatives. Polycarbonate/polycarbonate blends were also studied. The primary method for studying miscibility was differential scanning calorimetry. Dynamic mechanical analysis and infrared analysis were also utilized.

Blends of high molecular weight bisphenol-A polycarbonate (BPC) and tetramethylbisphenol-A polycarbonate (TMPC) were found miscible in all proportions at temperatures exceeding 300°C. The phase behavior of BPC blended with tetrachlorobisphenol-A polycarbonate (TCPC) was found to depend strongly on the molecular weight of the homopolymers. Low molecular weight blends exhibit LCST behavior. The remaining binary combinations of BPC, TMPC, TCPC, hexafluorobisphenol-A polycarbonate (HFPC), and tetrabromobisphenol-A polycarbonate (TBPC) form two-phase blends at all blend compositions between 20 and 80% by weight.

TCPC forms single-phase blends with PVC. Annealing temperatures up to 240^{o}C did not affect phase separation in these blends. Infrared analysis in the carbonyl stretch region does not implicate the carbonate group as a significant factor affecting miscibility in these blends. Dynamic mechanical analysis shows that the two polymers retain their own secondary relaxations.

TCPC is also miscible with solution-chlorinated PVCs (solution-CPVCs) having chlorine contents up to 70.2 weight percent, by weight, chlorine. Slurry-chlorinated PVCs were also miscible with TCPC. TBPC appears to be miscible with PVC and CPVCs, though it shows more an affinity for the chlorinated PVCs. Miscibility in these blends is favorable interactions with vinyl chloride monomer and/or a repulsive, intramolecular copolymer effect within the solution-CPVC.

Segmental interaction parameters, X_{ij}, were estimated using a binary interaction, mean field theory which can be applied to miscibility data from copolymer-containing blends. The boundaries of miscibility windows in polycarbonate-copolymer/solution-CPVC blends were used to calculate X_{ij}'s. Miscibility windows were shown to be sensitive to small changes in the X_{ij}.

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INTRODUCTION

Polymer blending has become an important method for producing materials with tailored properties. For example, to improve impact strength, a rubber modifier may be added to a brittle thermoplastic. This describes high-impact polystyrene (HIPS); styrene-butadiene-styrene block copolymer is added to form a dispersed, energy-absorbing rubber phase. Other advantages of blending polymers are (1) reduced material costs; (2) improved processing properties; (3) enhanced thermal and mechanical properties, such as heat distortion temperature, Young's modulus, toughness, etc.

In the last fifteen years much has been written on this topic. There have been several books[1-5] on polymer blends and innumerable studies in the literature. Blends of poly(vinyl chloride) (PVC) and chlorinated PVC (CPVC) with polycarbonates (PCs) have not yet received much attention. From a PVC applications perspective, miscible blends with PCs might broaden the range of PVC applications.

There are two objectives to this research. One is to investigate the use of polycarbonates as modifiers for PVC and CPVCs. Recent studies have suggested that increased halogenation of a polymer improves its miscibility with polycarbonates.[6,7] The second goal is to determine segmental interaction parameters, χ_{ij}'s, for CPVC/PC blend systems. With knowledge of the χ_{ij}'s, it may be possible to predict behavior of copolymer-containing blends. The interaction parameters will be determined using a mean field theory[8-10], an approach developed to explain miscibility in copolymer-containing blends.

Several topics will be discussed in this chapter. The properties of PVC, CPVCs, and PCs will be briefly described. This will be followed by a review of previous work on PC/(C)PVC blends. The last sections will contain discussions of polymer blend theory, estimation of segmental interaction parameters using the mean field approach, and criteria for judging blend miscibility.

Poly(vinyl chloride) (PVC) and Polycarbonate

Poly(vinyl chloride) (PVC) is among the most important commercial polymers. Its annual production exceeds that of most other commercial polymers with only polyethylene and polypropylene coming close.[11] Many books have been published on PVC properties and technology.[12-16]

PVC is a rigid material at room temperature; its glass transition temperature, T_g, ranges between 75°C and 90°C depending upon molecular weight. Above T_g there is a very broad melting region, extending from approximately 110° to

230°C. Such a broad transition indicates that crystal perfection is minimal, hence some consider PVC to aggregate rather than crystallize.[11] This tendency to aggregate or crystallize is great and has been observed in this study using differential scanning calorimetry (DSC). The degree of crystallinity found in PVC polymerized at normal temperatures is small, typically about 5%.[17] Highly syndiotactic samples, produced by polymerization below 0°C, may have crystallinities in excess of 40%.[11,17]

PVC aggregation/crystallization gives plasticized PVC its elastomeric properties. The aggregates act as crosslinks, imparting elastomeric character to the plasticized material.

Practical use of rigid PVC has limitations. The T_g of PVC is below 100°C, and this low glass transition temperature correlates with a low heat distortion temperature. This requires that rigid PVC use be restricted to relatively low temperature applications. Chlorination of PVC will raise the T_g.[11,18,19] CPVC is commercially available and is used in high temperature applications for which PVC is unsuitable.

PVC has poor thermal stability characteristics.[11,20,21] In air or in vacuum, PVC degrades at temperatures not far above the glass transition temperature. Defect structures introduced during polymerization are responsible for the instability. Such defects include carbon-carbon double bonds and branch structures having a labile, tertiary chlorine. The primary degradative process below 300°C is dehydrochlorination (Figure 1.1). While there is debate over the degradation mechanism, the result is the generation of polyene sequences in the PVC backbone with generation of HCl. Color changes accompany polyene formation. With time, at elevated temperature, a PVC film will change from transparent to black. Significant discoloration occurs at dehydrochlorination levels as low as 0.1%.[21] Temperatures at which degradation may occur are relatively low. For example, a transparent, clear PVC film (approximately 0.5 mm thick) having a T_g of 75°C was placed in a vacuum oven at 90°C. After three days this film had a purple tint. For this reason, PVC is compounded with stabilizers so processing will not damage the polymer.

Polycarbonate is an important specialty polymer. The term "polycarbonate" usually refers to the aromatic polycarbonate derived from bisphenol-A and phosgene, bisphenol-A polycarbonate, BPC (Figure 1.2). In this dissertation, "polycarbonate", or the abbreviation "PC", will refer to any aromatic polymer or copolymer derived from a bisphenol and phosgene. BPC has a high glass transition temperature (150°C), good toughness, and optical clarity. Commercial grade BPC has little tendency to crystallize from the melt, although exposure to solvent or solvent vapors may induce crystallization.[22,23]

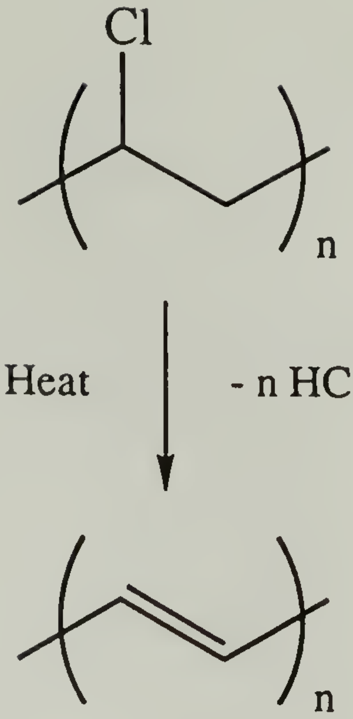

Figure 1.1. General scheme for PVC dehydrochlorination.

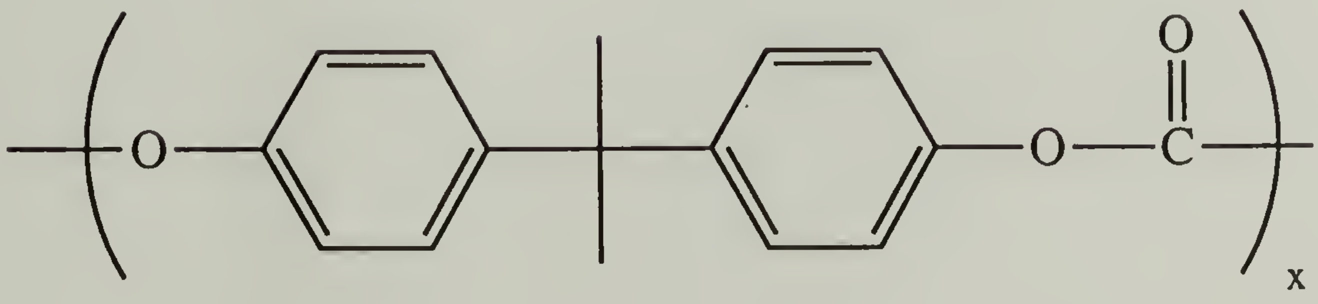

Figure 1.2. Repeat unit structure of bisphenol-A polycarbonate (BPC).

Since their discovery and commercial development in the 1950's, many polycarbonates have been synthesized and studied. Many are based on di- and tetra- substitutions on the phenyl rings of BPC. Replacement of the isopropylidene group and its effect on properties has also been investigated.[22-27] Many bisphenol-A-based polycarbonates have been found to be useful in applications ranging from flow modifiers to gas separation membranes.

PVC (CPVC) / Polycarbonate Blends

Despite the commercial significance of both PVC and polycarbonate (PC), little has been written of their blends with one another. Most of the literature on PVC/PC blends is found in patents. In this section the open and patent literature will be reviewed.

Hardt *et al.*[28] reported on the properties of tetramethylbisphenol-A polycarbonate (TMPC) blended with PVC. The TMPC-containing alloy investigated was a blend of PVC, TMPC, and high-impact polystyrene (HIPS). The Vicat softening temperature of the blends increased monotonically with increasing TMPC content. Dynamic mechanical analysis (DMA) of the system revealed a multiphase system with glass transitions for the rubber phase, the PVC phase, and a TMPC phase. The PVC T_g was shifted slightly higher than pure PVC. Transmission electron micrographs confirmed the phase separated structure; the rubber phase formed discrete spherical particles, while the matrix was also two phase, having a PVC-rich phase and a TMPC/PS-rich phase. These blends were transparent and the authors declared the system compatible.

Bisphenol-A polycarbonate (BPC) was blended with various halogenated polymers by Woo *et al.*[6] Among the chlorinated materials were PVC and Saran, a vinyl chloride-vinylidene chloride copolymer. Using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC), they showed that PVC/BPC was immiscible and Saran/BPC was miscible. The authors noted that phase behavior might be influenced by intramolecular interactions within the Saran copolymer.

Braun *et al.*[7] investigated the behavior of BPC and TMPC with PVC, a CPVC containing 60% by weight chlorine, and three vinyl chloride-vinylidene chloride copolymers having chlorine contents of 67.8, 70.4, and 71.4% (wt). PVC was found to be immiscible with both BPC and TMPC. TMPC was found to be "partially miscible" with the CPVC, and miscible with the remaining chlorinated polymers. BPC was only miscible with the vinyl chloride-vinylidene chloride copolymers. Fourier transform-infrared (FT-IR) analysis was employed to investigate the effect of blending on the carbonyl stretching region of TMPC. Shifts to lower wavenumbers were observed in TMPC blends with the CPVC and the copolymers. The magnitude of these shifts increased with decreasing TMPC content with the largest shifts, up to 9 cm^{-1}, occurring at 10% TMPC loading. Based on their IR results, the authors concluded that hydrogen-bonding interactions between the methyne hydrogen of PVC and the TMPC carbonyl group could not be responsible for miscibility since the number of these hydrogens decreases with increasing chlorine content. They speculated that dipole-dipole interactions involving the PC carbonyl group led to miscibility.

In another study, Braun *et al.*[29] used the same chlorinated vinyl polymers in blends with BPC, TMPC, and a 30/70 copolycarbonate of tetramethylbis(sulfone)/bisphenol-A (TMSPC). The purpose of the investigation was to determine the usefulness of ATR-FTIR as a tool in miscibility studies. TMSPC was found miscible with PVC. The IR data for TMSPC/PVC blends showed no shift in the carbonyl stretch region but the $-SO_2-$ peak did shift to lower wavenumbers. The magnitude of the shift increased with decreasing TMSPC content. IR results were not presented for TMSPC blended with the other chlorinated materials nor were they presented for other PC/chlorinated polymer blends.

Drzewinski[30] studied the "conformational effects" in PC/PVC blends brought about by substitution and copolymerization of BPC. It was reported that TMPC and a 70/30 copolymer of BPC and hexafluorobisphenol-A PC (HFPC) were miscible with PVC. Also, three other PCs--BPC, a 70/30 BPC/biphenyl copolymer, and a 50/50 BPC-phenyl ether copolymer--were found compatible with PVC, that is, these blends exhibited two T_g's which were shifted toward one another. DSC was used to determine blend behavior. Results were taken from second heats of samples initially heated to 275^{o}C. No details were provided regarding blend preparation or polymer molecular weights. From the PC T_g information (BPC = 142^{o}C, TMPC = 179^{o}C, 70/30 BPC/HFPC copolymer = 141^{o}C), it is obvious that the PCs are of very low molecular weight. This factor may explain the observed blend miscibility.

Recently, Termine[31] has reported on the use of oligomeric tetrabromobisphenol-A polycarbonate (TBPC) as a heat distortion modifier for PVC and CPVC. The glass transition temperatures of both PVC and CPVC increased linearly with increasing TBPC content. At 30% (by weight) TBPC, the T_g's of both PVC and CPVC increased by 20^{o}C. Heat distortion temperatures increased by nearly the same amount.

The patent literature has many entries referring to blends containing PVC and PCs.[32-41] Patents typically describe complex compound formulations. Nearly all patents containing these polymers also add polymeric modifiers such as block and graft copolymers.[32-38] These additives serve as processing aids and/or enhance the properties of the finished product. PVC is usually replaced by a "vinyl chloride polymer", indicating that the "PVC" used in the formulation may contain 80% or less vinyl chloride repeat units.

A polycarbonate cited frequently in the patent literature is that based on tetramethylbis(sulfone).[29,33, [34,39] In a patent by Robeson *et al.*[29], copolymers of bisphenol-A and tetramethylbis(sulfone) were synthesized. In the polymerization of random copolymers, 15% of the bisphenol-A would be reserved until nearly the end of the reaction. This would result in BPC blocks at the chain ends. They also synthesized an alternating copolymer. The random copolymers were 40/60 and 50/50 (mole/mole) bis(sulfone)/bisphenol-A. Blends of these polycarbonate copolymers with PVC were prepared with only the addition of a PVC stabilizer. Most blends were miscible, indicated by transparency of the blend and the presence of a single T_g. The one exception was a blend containing a high molecular weight 50/50 random copolymer which was partially miscible, having two T_g's that were shifted toward one another.

The Thermodynamics of Polymer Blends

The blending of polymers is an important area of research in polymer science. Reviews have appeared recently which discuss all aspects of blends, from theories to explain miscibility to the determination of miscibility from physical properties.[1-5] In this section some of the theories of polymer blends will be presented.

The Gibbs free energy change of mixing, G_M, will determine the phase behavior of a polymer blend. G_M may be expressed by

$$G_M = H_M - TS_M \qquad (1.1)$$

where H_M is the enthalpy of mixing, S_M is the entropy of mixing and T is the absolute temperature. A necessary condition for miscibility is $G_M < 0$. From Equation (1.1), negative heats of mixing and positive changes in the entropy with mixing will favor polymer mixing.

Scott[42] extended the Flory-Huggins equation[43,44] for the free energy of mixing polymer-containing systems

$$G_M/RT = (v_1/N_1) \ln v_1 + (v_2/N_2) \ln v_2 + X_{12} v_1 v_2 \quad (1.2)$$

where R is the gas constant, v_i and N_i are the volume fraction and degree of polymerization, respectively, of component i, and X_{12} is the Flory-Huggins interaction parameter. The first two terms on the right hand side of Equation (1.2) are combinatorial entropy terms. For polymers, N_i is large and these terms become negligible. The X_{12}-term is an enthalpic contribution due to contact energy dissimilarities. Because X_{12} is inversely proportional to temperature, its magnitude decreases as temperature increases. In the derivation of Equation (1.2), X_{12} is assumed to have no composition dependence.

The Flory-Huggins theory is only able to predict upper critical solution temperature (UCST) behavior. To improve the Flory-Huggins theory, Koningsveld and Kleintjens[45] redefined the interaction parameter, g, to have both composition and temperature dependence

$$g = g_0 + g_1/T + g_2T + g_3\ln T \qquad (1.3)$$

where the g_i can be assigned concentration dependence to fit the data. The g_i in Equation (1.3) are empirical parameters. Temperature dependence of the interaction parameter allows the Flory-Huggins equation to predict lower critical solution temperature (LCST) behavior. The concentration dependence allows the shape of the spinodal curve to deviate from a symmetric curve, for example, to simulate systems with multiple critical points. Other empirical models for the interaction parameter, having both temperature and concentration dependence, have also been developed.[46]

Use of Equation (1.2) requires the reinterpretation of X_{12} as a free energy parameter composed of enthalpic and non-combinatorial entropy contributions.[47] This is necessary because the Flory-Huggins theory (1) does not account for the non-random effects during mixing such as formation of hydrogen bonds between molecules; (2) neglects volume changes upon mixing in the derivation of Equation (1.2); and (3) neglects "free volume", or "equation-of-state", effects. Coleman and Painter[48] have added a free energy correction term to Equation (1.2). In their approach, X_{12} is calculated from the solubility parameter method.[49] Thus X_{12} is always positive and unfavorable to mixing. The correction term includes enthalpic effects due to specific interactions.

Equation-of-state theories have been proposed to predict polymer solution and polymer blend behavior.[50-53] In these theories the blend phase behavior is dependent upon the pure component properties. The critical temperature, pressure, and specific volume (T^*, P^*, v^*) of the components are calculated from the thermal expansion coefficient, thermal pressure coefficient, and specific volume. Mixing rules define the blend properties based on those of the pure components.

Application of these equation-of-state theories allows for the enthalpic contribution to the free energy to be estimated. For example, the lattice fluid theory of Sanchez and Lacombe has been used to determine the interaction parameter from cloud point behavior in binary polymer blends.[54-56] By equating the cloud point curve to the spinodal, a necessary assumption, the interaction parameter becomes the fitting parameter for the spinodal equation.

A necessary condition for miscibility is a G_M value less than zero. This, however, is not sufficient to guaranty miscibility. For phase stability in the Flory-Huggins treatment, the second derivative of G_M with respect to composition, d^2G_M/dx_i^2., x_i being a composition variable, must be positive. In the equation of state approach, another term is added to this inequality[57]

$$d^2G_M/dx_i^2 - vB(d^2G_M/dx_i dv)^2 > 0 \qquad (1.4)$$

v is volume and B is the isothermal compressibility. Because $(d^2G_M/dx_2dv) > 0$ and B increases with temperature, this term destabilizes the blend and leads to phase separation at high temperatures.

Copolymer-Containing Blends

Over the last decade, much research has focused on blends which contain random copolymers. It has been recognized that copolymerization may induce miscibility. For example, a homopolymer poly(A) may be blended with a copolymer, poly(B-co-C). Even though the binary combinations of homopolymers poly(A), poly(B), and poly(C) may be immiscible, there may exist a range of copolymer compositions of poly(B-co-C) which will be miscible with poly(A).

To account for this phenomenon, a binary interaction, mean field theory has been developed.[8-10] The Flory-Huggins form of the free energy function is retained and χ_{12} of Equation (1.2) is generalized and referred to as χ_{blend}. Consider a blend of two copolymers. Copolymer 1 is composed of A and B repeat units $(A_{1-x}B_x)$; copolymer 2 is composed of C and D units $(C_{1-y}D_y)$. x and y are the volume fractions of B and D units, respectively, within each copolymer. χ_{blend} may be written

$$\chi_{blend} = xy\chi_{BD} + (1-x)y\chi_{AD} + x(1-y)\chi_{BC} + (1-x)(1-y)\chi_{AC} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD} \qquad (1.5)$$

where χ_{ij} are the segmental interaction parameters. χ_{blend} depends on both intermolecular and intramolecular interactions. Equation (1.5) shows that all six χ_{ij} values may be positive--unfavorable for mixing--yet a negative χ_{blend} will result if the intramolecular "repulsion", described by the sum of the χ_{AB}- and χ_{CD}-terms, is of sufficiently large magnitude.

For the two-copolymer system described above, an isothermal "miscibility map" can be constructed as shown in Figure 1.3. The abscissa and ordinate correspond to the fraction of monomer B in copolymer 1 and the fraction of D in copolymer 2, respectively. The corners of the diagram represent binary, homopolymer blends. The blend composition for this diagram is the critical composition, which is 1:1 by volume for very high molecular weight polymers. For this fictitious copolymer blend system, none of the homopolymers are miscible when blended. However, there is miscibility at certain copolymer compositions. The boundary between miscible and immiscible regions is elliptical in this example. Similar behavior has been reported by Huh and Karasz[58] for CPVC/butadiene-acrylonitrile copolymer blends.

To this point, the development of this theory has focused on the formation of a window of miscibility. The opposite case is theoretically possible as well; that is, the formation of an immiscibility window in copolymer blends in which the homopolymer blends at the corners of the

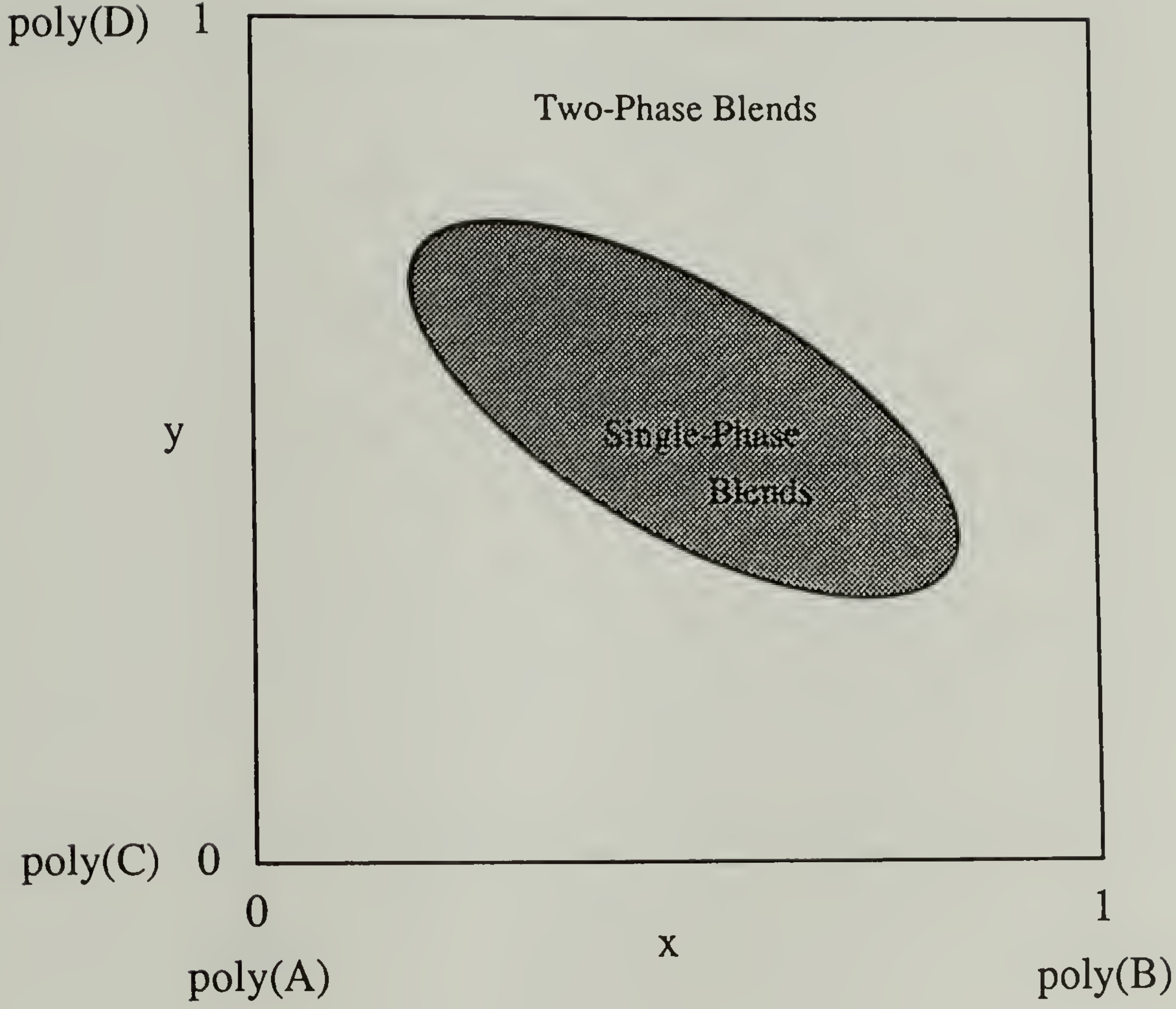

Figure 1.3. Isothermal miscibility map for an $(A_{1-x}B_x)/(C_{1-y}D_y)$ copolymer/copolymer blend. Blend composition is constant. Shaded area represents a "miscibility window".

miscibility map are miscible. Blends of poly(vinyl chloride-*co*-vinyl acetate) and poly(*n*-butyl methacrylate-*co*-isobutyl methacrylate) have been shown to exhibit this behavior.[59]

The χ_{ij}'s can be calculated from the miscibility/immiscibility boundary of the miscibility map.[60] At this boundary, $\chi_{blend} = \chi_{critical}$, where

$$\chi_{critical} = (1/2)(N_1^{-1/2} + N_2^{-1/2})^2. \tag{1.6}$$

A function f can be defined

$$f = \chi_{blend} - \chi_{critical}. \tag{1.7a}$$

The value of f will determine the phase behavior at any point on the miscibility map:

$f > 0$ immiscible (1.7b)

$f = 0$ boundary (1.7c)

$f < 0$ miscible. (1.7d)

Equation (1.5) for χ_{blend} is a quadratic function and Equation (1.7a) can be written in a generalized form

$$f = Ax^2 + Bxy + Cy^2 + Dx + Ey + F \tag{1.8}$$

where the coefficients A through F are functions of the χ_{ij}'s and $\chi_{critical}$

$$A = \chi_{AB} \tag{1.9a}$$

$$B = \chi_{AC} + \chi_{BD} - \chi_{AD} - \chi_{BC} \tag{1.9b}$$

$$C = \chi_{CD} \tag{1.9c}$$

$$D = \chi_{BC} - \chi_{AC} - \chi_{AB} \tag{1.9d}$$

$$E = \chi_{AD} - \chi_{AC} - \chi_{CD} \tag{1.9e}$$

$$F = \chi_{AC} - \chi_{critical} \tag{1.9f}$$

Equation (1.8) may describe an ellipse, a hyperbola, or a parabola. The equation for the ellipse which fits the boundary in Figure 1.3 is used to calculate the χ_{ij}'s. Before solving for the χ_{ij}'s, two pieces of information are needed: $\chi_{critical}$, which is determined from molecular weight data, and one of the χ_{ij}'s, which must be determined independently.

In this research both PC homopolymers and copolymers have been blended with PVC and CPVCs. Modeling CPVC as a copolymer, the mean field approach described above will be used to determine segmental interaction parameters in the PC/PC and CPVC/PC blend systems. Interaction parameters for polycarbonate repeat units will also be determined from PC copolymer blend data. The calculated values will be compared for self-consistency.

Criteria for Miscibility

There are several methods which can be used to assess miscibility in a blend. An amorphous miscible blend will form a transparent film; at the phase separation temperature, the film will become cloudy if the refractive index difference between the components is greater than 0.004.[7] NMR spin diffusion and infrared spectroscopy also can be used to study miscibility. Thermal properties measured by differential scanning calorimetry, dynamic mechanical analysis, or dielectric thermal analysis are also used; the presence of a single T_g intermediate to the component T_g's indicates a miscible blend.

The primary means of evaluating miscibility in this investigation was the presence of a single T_g for a blend determined through DSC experiments. This technique has advantages which make it particularly useful to this study. First, sample sizes are minimal, usually 5-15 mg. This is helpful because the quantity of material was limited. Second, high heating and cooling rates (up to 320^{o}C/minute) are possible. PVC and CPVCs are heat sensitive and exposure to high temperatures--tempertures above T_g--must be kept to a minimum. Preliminary thermal treatments of blend samples, such as annealing, utilized heating/cooling rates of 100-200^{o}C/minute. These high rates assured that the sample was at high temperatures for only the prescribed amount of time. Second heats, from which miscibility was assessed, were carried out at rates of 20 to 40°C/minute. The rates were chosen so that degradation would be minimized.

In addition to DSC, dynamic mechanical analysis (DMA) was also used for blend characterization. Besides the relaxation due to the glass transition, secondary relaxations in the glassy state are detected. These relaxations arise from local segmental motion originating from side groups or within the main chain.[61] These processes provide clues about the degree of mixing. For example, intimate mixing on a molecular scale may lead to an antiplasticizing effect which reduces the magnitude of the secondary relaxation.

Experimental Methods

Differential Scanning Calorimetry (DSC). Measurements were done on a Perkin-Elmer System 7 under a dry nitrogen purge. All annealing pretreatments were done in the DSC cell. Typical sample weights ranged from 5 to 15 mg. Different scan rates were utilized to minimize degradation; 20°C/minute and 40°C/minute were the most commonly used rates. Indium and zinc were used to calibrate the instrument.

Dynamic Mechanical Analysis (DMA). A Polymer Laboratories DMTA Mk I was used to study changes in modulus and mechanical loss tangent as a function of temperature and frequency. The temperature range available on this instrument is -140°C to 500°C. The frequency range used was

0.1 to 10 Hz. Samples were rectangular films or bars mounted in a single cantilever mode. For some of the low molecular weight materials, coating onto aluminum foil or glass filter paper provided support to facilitate measurement.

FT-IR. Fourier transform infrared analysis was used to characterize the materials and some blends. A Nicolet Instruments IR Spectrometer was used. Samples were either free standing films or were cast from solution onto KBr plates. Measurements were made at 1, 2 or 4 cm^{-1} resolution with 32 (64 at 1 cm^{-1} resolution) scans per measurement.

Thermogravimetric Analysis (TGA). These experiments were carried out on a Perkin-Elmer System 7 thermogravimetric analyzer. All runs were done under dry nitrogen. Typically, a thermal scan rate of $20^{o}C$/minute was used to determine weight loss as a function of temperature. For isothermal operation, a rate of $200^{o}C$/minute was used to reach the target temperature.

Gel Permeation Chromatography (GPC). GPC was used to characterize the molecular weights of the materials used in this investigation. This technique was also used to study degradation effects in blends. THF was the solvent; the column temperature was $30^{o}C$. The detection system was a Waters 410 Differential Refractometer and analysis of the data was performed by the Waters Data Module. The system was calibrated using polystyrene standards from Polymer Laboratories. Reported PVC, CPVC, and PC molecular weights are relative to these polystyrene standards. Polycarbonate molecular weights relative to polycarbonate resin (BPC), secondary standards from Aldrich (Product number 18,167-6) were found to be one-half the PS-standard value.

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CHAPTER 2

CHARACTERIZATION OF POLY(VINYL CHLORIDE), CHLORINATED POLY(VINYL CHLORIDE), AND POLYCARBONATES

To understand polymer blend behavior, it is necessary to know the properties of the component materials. Of particular interest are the thermal properties derived from differential scanning calorimetry (DSC), since this analytical technique was the primary means of assessing blend miscibility. DSC is used to determine the glass transition temperature of polymers and their blends. In addition to DSC, several other techniques were used to characterize the polymers, such as gel permeation chromatography (GPC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and Fourier transform-infrared analysis (FT-IR).

Poly (Vinyl Chloride)

PVC samples were obtained from three sources: B. F. Goodrich (PVC-0), LARK Enterprises (PVC-1), and Aldrich Chemical (PVC-2). The molecular weight and thermal characteristics of these materials are given in Table 2.1.

Table 2.1. Characterization of PVCs and CPVCs.

	wt % Cl	$M_n(10^3)$	M_w/M_n	M_z/M_w	T_g (°C)	ΔC_p (J/gK)
PVC						
PVC-0	56.7	22.3	2.66	1.89	76	0.350
PVC-1	56.7	56.9	2.09	2.01	86	0.295
PVC-2	56.7	108.0	2.28	1.74	90	0.290
Solution-Chlorinated PVC						
CPVC-1	58.3	63.3	2.21	2.48	88	0.304
CPVC-3	59.2	67.7	2.12	2.29	91	0.315
CPVC-4	60.0	68.7	2.11	2.45	95	0.322
CPVC-5	61.4	71.7	2.10	2.48	100	0.320
CPVC-6	62.2	72.1	2.03	2.25	106	0.283
CPVC-7	63.5	68.5	1.94	2.09	115	0.272
CPVC-8	65.4	69.4	1.82	1.80	127	0.225
CPVC-9	67.3	69.5	1.90	1.74	147	0.197
CPVC-10	69.2	62.1	1.90	1.71	178	0.161
CPVC-11	70.2	54.8	1.97	1.76	195	0.159
CPVC-12	70.6	48.1	1.95	1.82	211	0.150
Slurry-Chlorinated PVC						
BFG-63	63.5	33.3	2.08	1.79	107	0.260
DSP-63	63.5	29.0	2.30	1.76	106	0.260
BFG-68	68.3	25.1	2.53	1.90	130	0.230
DSP-68	68.3	24.1	2.64	1.84	130	0.200

PVC samples were tested as received and as solvent-cast films; there was no effect on the thermal properties due to sample preparation. Solvents were methylene chloride (PVC-0) and tetrahydrofuran (PVC-1, PVC-2). Spectroscopic grade solvents were used without further purification.

The glass transition temperature is seen to vary with molecular weight. All PVC samples exhibited a broad melt endotherm above the T_g (Figure 2.1), including the solvent-cast samples which were optically clear. The small size and imperfect nature of the PVC crystallites is responsible for its melt behavior and the transparency of the PVC films.

The dynamic mechanical loss tangent of PVC-0 at 1 Hz is shown in Figure 2.2. The sample was prepared by pressing the powdered PVC at 160°C for 12 minutes in a Carver press. The peak at 86°C is associated with the glass transition. The temperature shift relative to the DSC T_g (Table 2.1) is due to the frequency dependence of the glass transition. Glass transition temperature increases with increasing frequency.[1,2] Below the T_g, there is a broad transition which peaks at approximately -33°C. This secondary relaxation, or *beta*-relaxation, begins below -100°C and ends near 40°C, immediately before the onset of the T_g peak. This transition is due to local segmental motion, perhaps involving 5 to 7 repeat units.[2]

The width of this low temperature relaxation may be explained in terms of the bulk structure of PVC. At 160°C, the sample processing temperature, both amorphous and

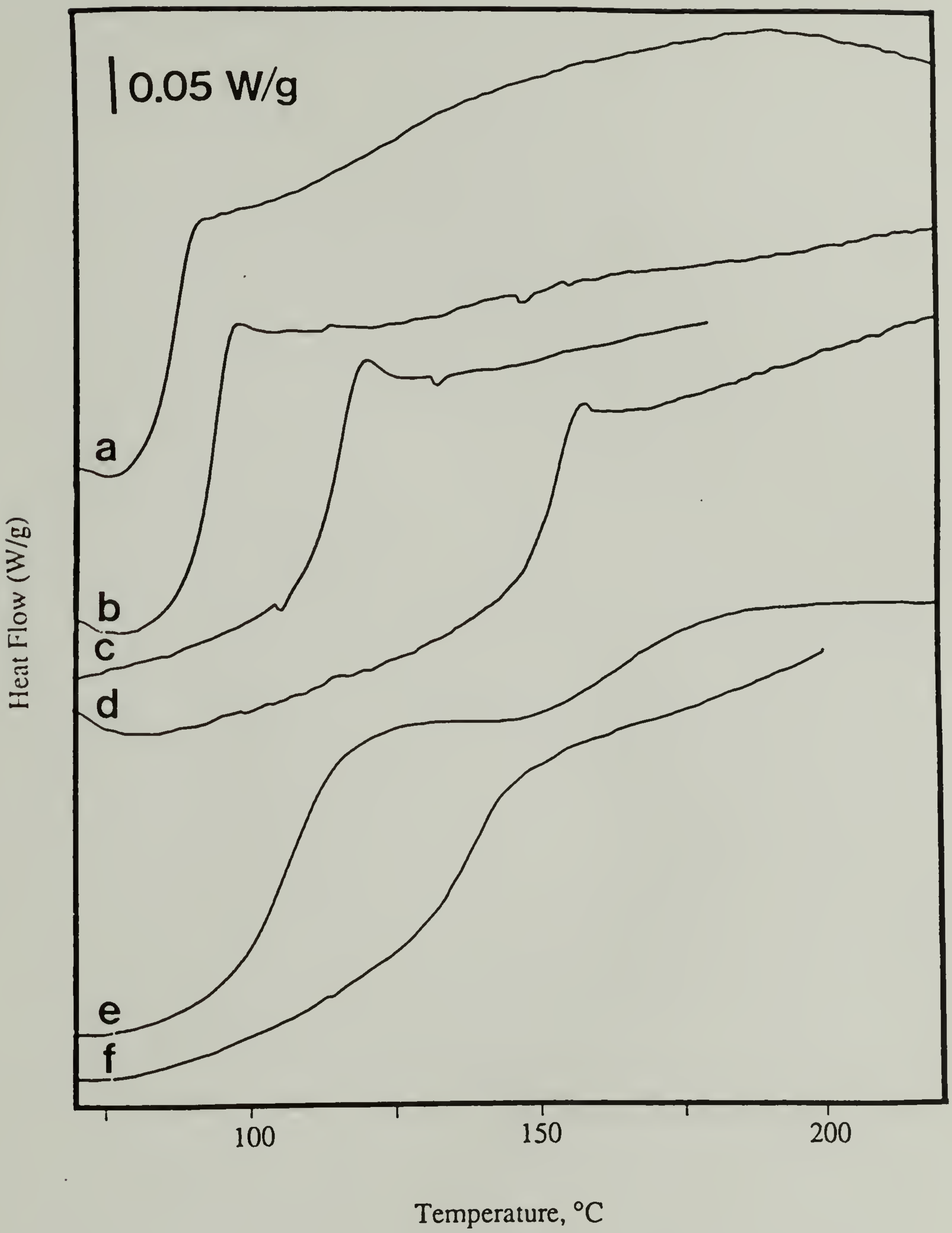


Figure 2.1. Effect of chlorination on PVC glass transition temperature as measured by DSC. a, PVC-1; b, CPVC-3; c, CPVC-7; d, CPVC-9; e, BFG-63; f, BFG-68.

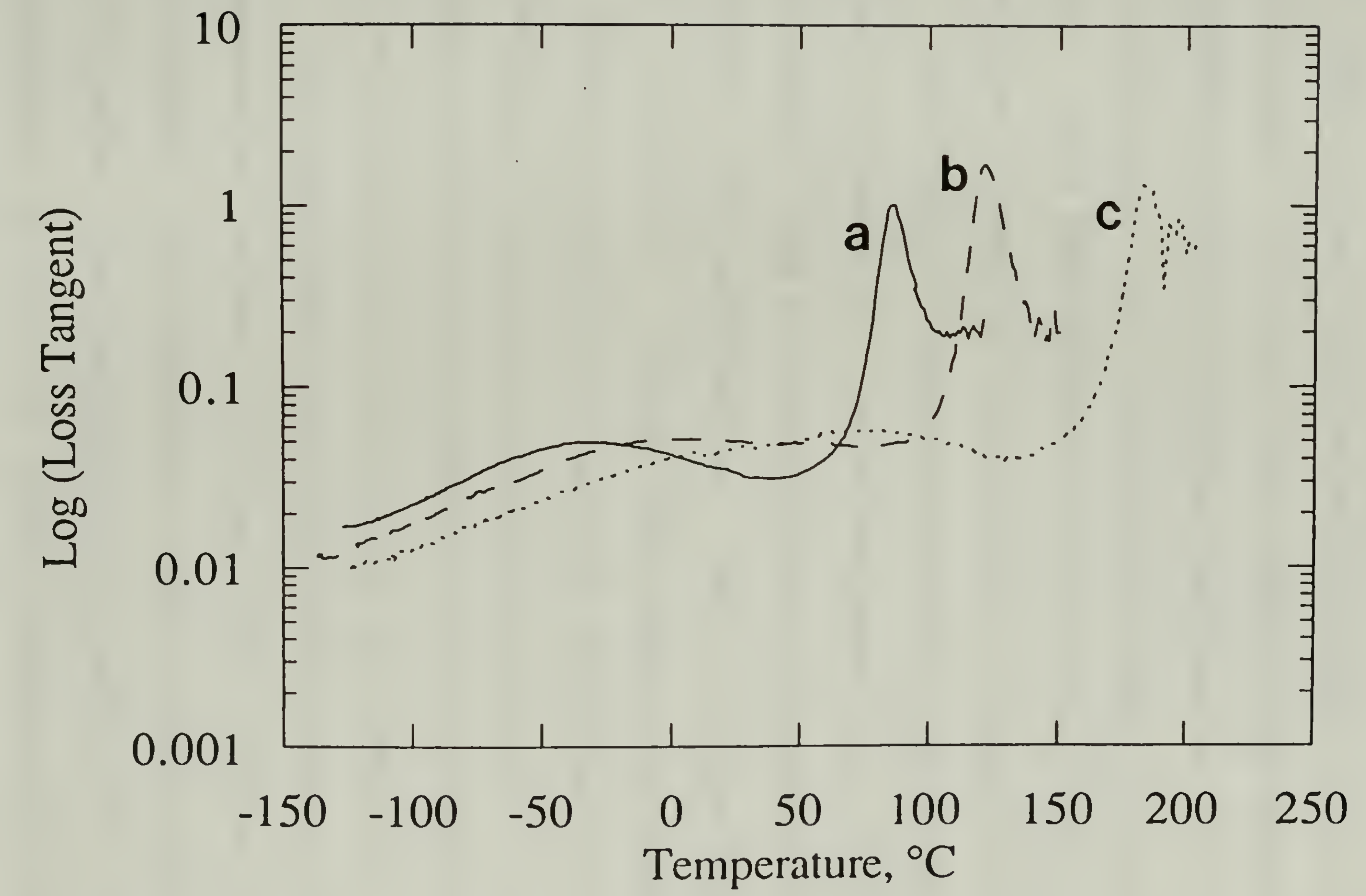


Figure 2.2. Dynamic mechanical loss tangent versus temperature for (a) PVC-0, (b) CPVC-7, and (c) CPVC-10. Measurement frequency is 1 Hz.

crystalline phases are present. The DMA response is therefore a composite of amorphous and crystalline phase behavior. The broad, *beta*-peak is a superposition of amorphous-phase and crystalline-phase relaxations.

Activation energies, E_a, for the primary (T_g) and secondary relaxations can be determined from multifrequency experiments. With the peak temperatures being frequency dependent, a plot of inverse temperature (1/K) versus log(frequency) has a slope proportional to E_a (an Arrhenius plot). E_a's were found to be 609 kJ/mol and 90 kJ/mol for the glass transition and secondary relaxation, respectively.

The Fourier transform-infrared results for PVC-0 are shown in Figure 2.3. Peak assignments for PVC have been discussed[3-7] and have been found to be sensitive to tacticity and conformation. The C-Cl stretch region is 600 cm^{-1} to 800 cm^{-1}. Within this region, the isotactic stretch is found at 610-630 cm^{-1} and the syndiotactic C-Cl stretching vibration is located at 690 cm^{-1}.[7] Discussions concerning IR band assignments will be presented later, when PVC and chlorinated PVCs spectra are compared.

TGA measurements show that PVC starts to lose weight at temperatures between 250°C and 300°C (Figure 2.4). In these experiments, the temperature was increased at a rate of 20°C/minute. The degradation proceeds via a two-step mechanism. In the first step, between 250°C and 400°C, dehydrochlorination is the primary process. Between 400°C

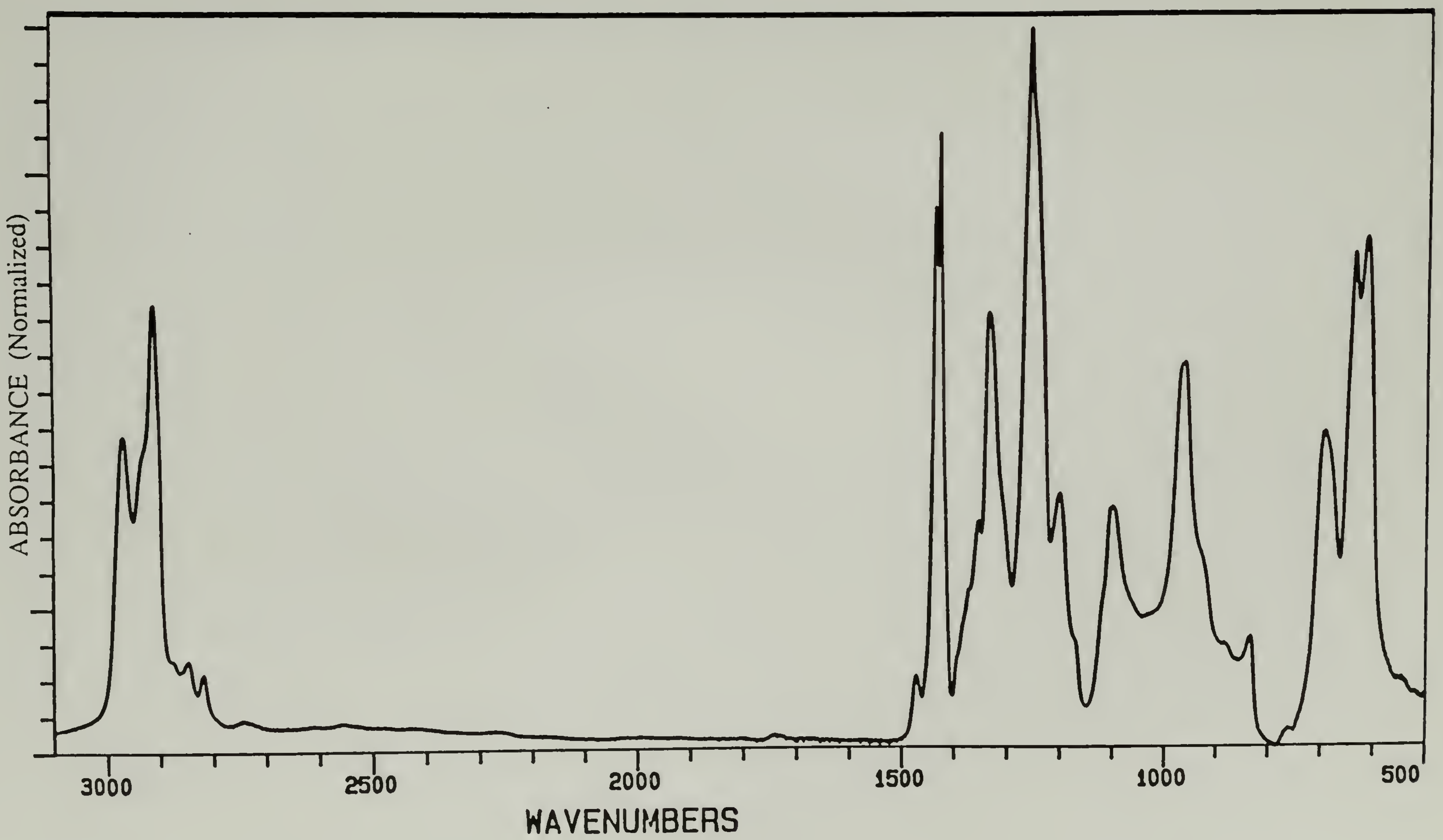


Figure 2.3. FT-IR spectrum of PVC-0.

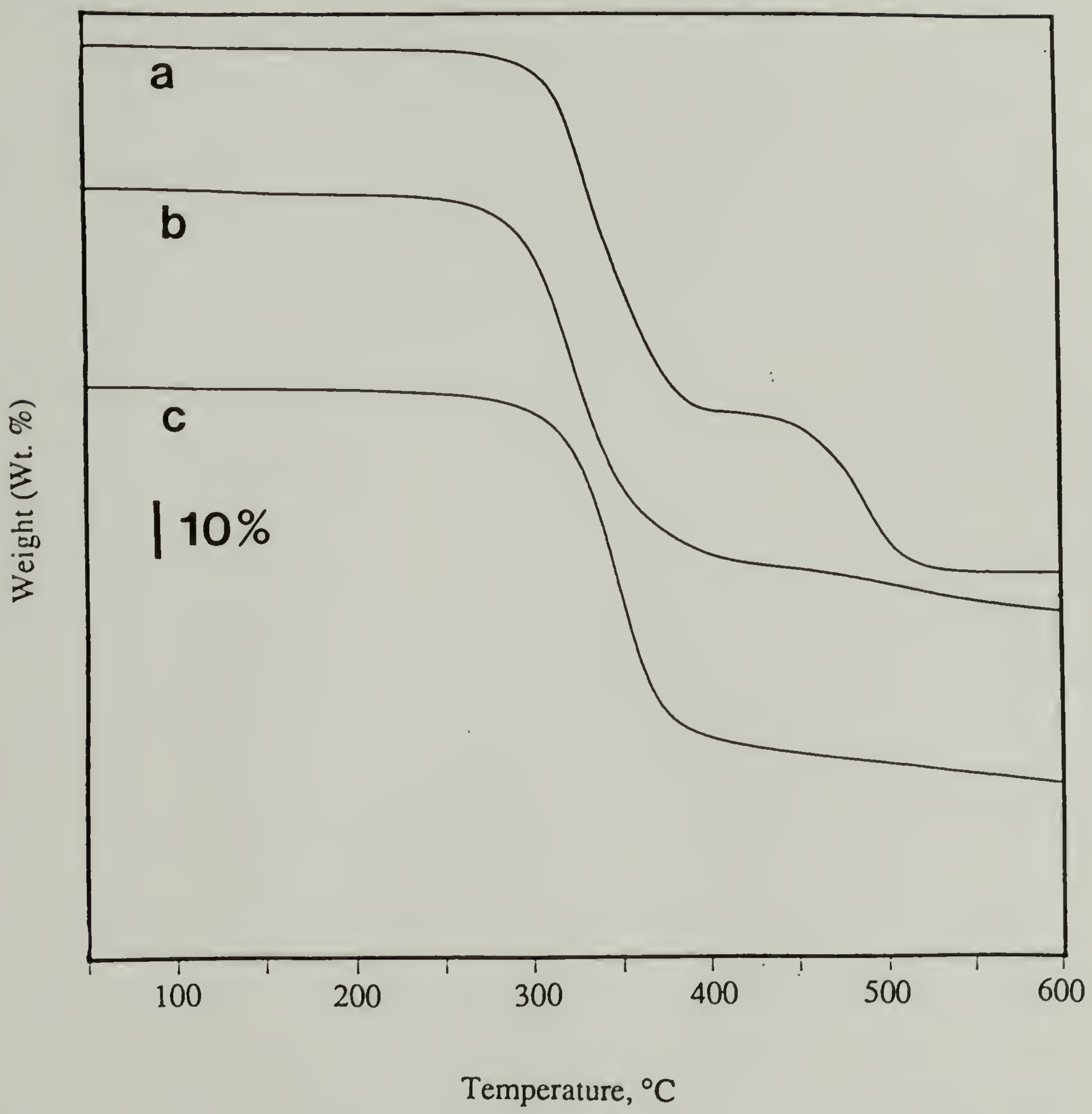


Figure 2.4. Weight loss as a function of temperature for (a) PVC-0, (b) CPVC-6, and (c) CPVC-10.

and 500^{o}C, reactions involving the polymer backbone take place, evolving volatiles such as benzene.[8,9]

Solution-Chlorinated PVCs

Solution-chlorinated PVCs (solution-CPVCs) were obtained from LARK Enterprises (Webster, MA). The starting resin for the CPVCs was a PVC obtained from SP^2 (Catalog no. 038Sb) having M_n = 57,300 and M_w = 122,300 (the molecular weight averages quoted by SP^2). Chlorination was accomplished by dissolving the PVC in chlorobenzene, then bubbling in chlorine while the reactor flask was irradiated by a 300 W tungsten lamp. At regular intervals, aliquots of solution were removed and precipitated in methanol. The polymer was redissolved in THF and precipitated once again in methanol. The precipitate was dried in a vacuum oven at 60^{o}C. Elemental analysis was performed by the University of Massachusetts Microanalysis Laboratory to determine the amounts of carbon, hydrogen, and chlorine in each of the CPVCs.

A few of the low chlorine content solution-CPVCs (< 59% chlorine) had a pale blue tint. This was probably caused by dehydrochlorination during the vacuum drying. This form of degradation occurs at moderate temperatures, and vacuum conditions drive the reaction toward further HCl production.

The molecular weights of the solution-CPVCs were determined by GPC. The results are given in Table 2.1. The molecular weights are relative to polystyrene standards obtained from Polymer Laboratories. The measured values for the PVC compare well with those reported by SP^2. It is of interest to note the trend in molecular weight as a function of chlorination. Small amounts of chlorination increase the molecular weight (hydrodynamic volume measured by GPC) of the material. This increase may be due to two effects. The replacement of a hydrogen with chlorine atom leads to restricted motion about the C-C bond. This steric effect results in fewer available conformations and increases the hydrodynamic volume of the CPVC. Also, the excess chlorination disrupts the tendency of PVC to self-associate. Free of this interaction, the chain would be free to assume more extended conformations. At high degrees of chlorination, chain scission may be responsible for the reduction in molecular weight.

Figure 2.1 shows the DSC results for some of the LARK CPVCs. The breadth of the glass transition--the difference between the onset and completion of the transition--is narrow, less than 11^{o}C, for the PVC and the CPVCs. For the solution-chlorinated PVC samples, this feature suggests that the excess chlorination is uniformly distributed along the PVC backbone. The PVC melt endotherm disappears with only a small addition of chlorine (< 2.5% wt excess). The CPVC containing 59.2% Cl (curve b in Figure 2.1) shows no indication of crystallinity; the melt endotherm is absent. The addition of a small quantity of chlorine is sufficient to disrupt crystallite formation. The DSC data for the solution-CPVCs are summarized in Table 2.1.

The glass transition temperatures of the CPVCs increase monotonically with increasing chlorine content. Also, the specific heat increment at T_g decreases as chlorine content increases. Both effects are attributable to the stiffening of the polymer backbone with the addition of chlorine. The initial increase in the specific heat increment with chlorination is due to decreased crystallinity, which results in a larger fraction of amorphous material. These results are consistent with the results of Lehr *et al.*[10] in which the thermal properties of CPVCs were investigated.

The dynamic mechanical spectra are similarly affected by the addition of chlorine. Both the glass transition and *beta*-relaxation temperatures increase with excess chlorination (Figure 2.2). The smaller magnitude of the PVC loss tangent peak at T_g, relative to the chlorinated PVCs, is due to PVC semicrystallinity. The glass transition is a phenomenon associated with the amorphous phase. In PVC, the portions of the polymer chain which are in the crystalline phase will not contribute to the T_g behavior. The CPVCs are amorphous, and the entire polymer will undergo the relaxation.

The magnitude of the low temperature, *beta*-relaxation is little affected by the addition of chlorine. While the temperature of the peak increases with chlorine content, the peak magnitude is nearly constant at approximately 0.070 for PVC and solution-CPVCs.

The degradation behavior of the CPVCs was investigated using thermogravimetric analysis (TGA). This technique was used for "as received" samples as well as for solution-cast films. In the latter case, TGA was also used to determine the residual solvent content of the film. Weight loss as a function of temperature for some solution-CPVCs is shown in Figure 2.4. The thermal instability of PVC and CPVC are seen in the Figure. Weight loss becomes evident above 250°C. By 300°C, significant weight loss has begun. The mechanism for PVC weight loss in the temperature range 200-400°C is dehydrochlorination. A second mode, between 400° and 500°C, involves the decomposition of the main polymer chain, resulting in the formation of volatiles and char.[8,9] Degradation of the chlorinated PVCs begins at the same temperature as PVC, though it is apparent that the dehydrochlorination step is affected by the presence of additional chlorine. This should be expected since the number of consecutive vinyl chloride, VC, ($-CH_2-CHCl-$) monomer residues decreases as chlorine is added to the methylene groups. Shorter sequences disrupt polyene formation. While the CPVCs begin to lose weight at the same temperature as PVC, they do not undergo the second mode of degradation observed for PVC. In the single, CPVC decomposition step, dehydrochlorination and other main chain degradation reactions must be occurring simultaneously. The addition of a liquid stabilizer, Advastab TM-181 (Thiokol-Carstab, Cincinnati, OH), did not change the TGA results.

Isothermal TGA experiments were done to examine thermal degradation as function of time. The results of these investigations were important for determining the feasibility of using high glass transition temperature polycarbonates as modifiers for PVC and CPVCs. Experiments were carried out at 230°C and 260°C on PVC-1, CPVC-6, and CPVC-10. Weight loss is nearly linear in the first 30 minutes. At 230°C, weight loss after 20 minutes for PVC and CPVC-10 was less than 3%. CPVC-6 had a 5% weight loss. At 260°C, weight loss was 10%, 15%, and 30% for CPVC-10, PVC, and CPVC-6, respectively. In Figure 2.4, CPVC-6 appears to start losing weight at a lower temperature than the other two samples. This may be due to defect structures introduced during the chlorination process and subsequent handling.

The infrared spectra of two of the CPVCs are shown in Figure 2.5. The C-Cl stretch vibrations are found in the 600-800 cm^{-1} region. The addition of chlorine to PVC is seen to affect the IR spectra profoundly. The absorptions in the C-Cl stretch region increase in intensity relative to the various CH vibrational modes (2800-3100 cm^{-1} and 1150-1500 cm^{-1}). The change in the C-Cl region from two peaks--one at 700 cm^{-1} and the other, a doublet, at 615 and 640 cm^{-1}--to a single peak at 690 cm^{-1} is consistent with previously reported results.[7,11]

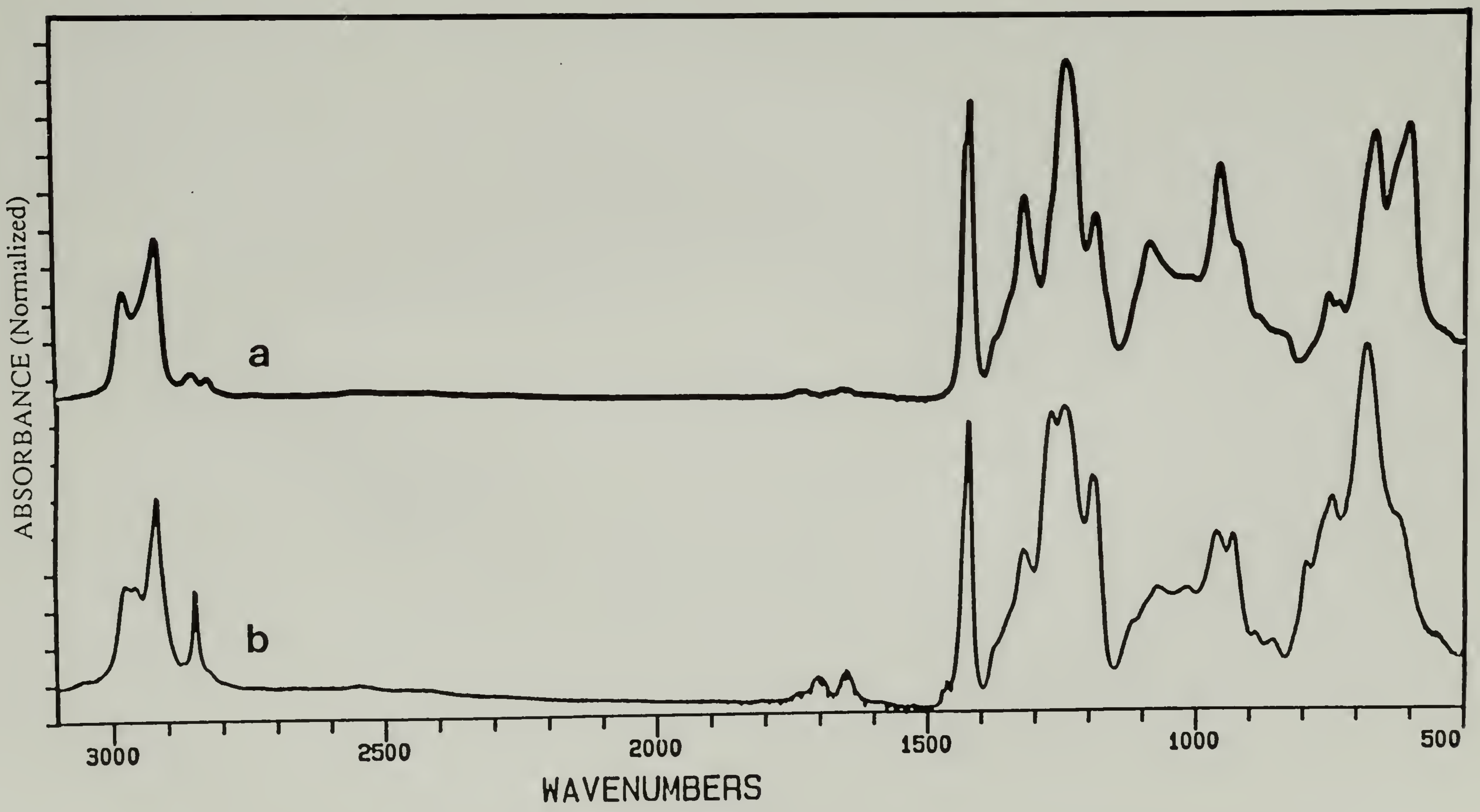


Figure 2.5. FT-IR absorption spectra of solution-chlorinated PVCs. (a) CPVC-4 and (b) CPVC-8.

Komoroski *et al.*[12] studied the microstructure of PVC and CPVC using ^{13}C-NMR. NMR shows that chlorine adds to $-CH_2-$ groups almost exclusively in the early stages of chlorination (< 60 % Cl by weight). From 60 to 70 wt % Cl, the percentage of $-CCl_2-$ groups increases linearly from 0% to approximately 8%. The percentages of -CHCl- and $-CH_2-$ groups change linearly with chlorine addition, increasing and decreasing, respectively.

In the discussions of blends containing solution-CPVCs, these polymers will be considered copolymers of vinyl chloride (VC, $-CH_2-CHCl-$) and 1,2-dichloroethylene (DCE, -CHCl-CHCl-). This assumption is valid, based on the small content of $-CCl_2-$ groups in the solution chlorinated PVCs.

Slurry-Chlorinated PVCs

The B. F. Goodrich Company, Geon Division, generously provided five samples for use in this investigation: one PVC sample (PVC-0), two CPVC samples having 63.5% chlorine (BFG-63, DSP-63), and two CPVC samples having 68.5% chlorine (BFG-68, DSP-68). Each CPVC sample was provided in unstabilized and stabilized forms. Disodium phosphate (DSP) was the stabilizer additive. Elemental analysis of the slurry-chlorinated PVCs confirmed the chlorine content quoted by Goodrich.

The molecular weight characteristics of these materials were determined using GPC. The results are summarized in

Table 2.1. These materials have a lower molecular weight than the solution-CPVC samples.

Slurry chlorination processes are much different from solution chlorination.[9] The former is a multiphase (heterogeneous) process whereas the latter is a single-phase process (homogeneous). Unlike solution chlorination, in which the entire PVC molecule is accessible to chlorine, slurry processing involves the chlorination of undissolved, PVC particles. Consequently, PVC on the surface of a particle becomes highly chlorinated while the PVC within the particle core may be free of additional chlorination. This difference in chlorine distribution leads to marked differences between the properties of solution and slurry chlorinated PVCs.

Differences between solution and slurry chlorination can be seen in the thermal behavior of the CPVCs as shown by DSC. Figure 2.1 shows the DSC traces for the slurry-chlorinated PVCs (slurry-CPVCs) and solution-CPVCs. The DSC behavior of the Goodrich CPVCs is different from the corresponding solution-chlorinated material having the same chlorine content. Notable is the presence of the melt endotherm in BFG-63. The endotherm is due to the presence of residual vinyl chloride sequences in the slurry-chlorinated material. These sequences are long enough to allow PVC crystallization to occur in the CPVC. The degree of crystallinity decreases with increasing chlorination;

this is reflected in the decrease in area of the melt endotherm peak.

Glass transition is also affected by the chlorination method. For a given weight percentage of chlorine, the T_g of a slurry-chlorinated CPVC is lower than its solution-chlorinated counterpart. This discrepancy may be partially accounted for by molecular weight difference between the samples. However, this may not explain such a large difference in the T_g's of the more highly chlorinated CPVCs.

The breadth of the glass transition region increases with increasing chlorination level in the slurry chlorinated samples. This effect reflects the high degree of heterogeneity in the polymer chain. The slurry-chlorinated material resembles a block copolymer of PVC and highly chlorinated PVC. The difference at high chlorine loading is especially significant. The microstructure of the slurry-CPVCs which leads to a broad glass transition is also responsible for decreasing the T_g, relative to solution-CPVC, at high chlorination levels.

The dynamic mechanical loss tangent of the slurry-CPVCs are in Figure 2.6. The measurement frequency is 1 Hz. The loss tangent peaks at T_g are wider for the slurry-CPVCs than for the solution-CPVCs. The broadened glass transition was also noted in the DSC results and is due to the differences in chlorine distribution.

The TGA data for these materials show that the degradation behavior is similar to the solution-chlorinated

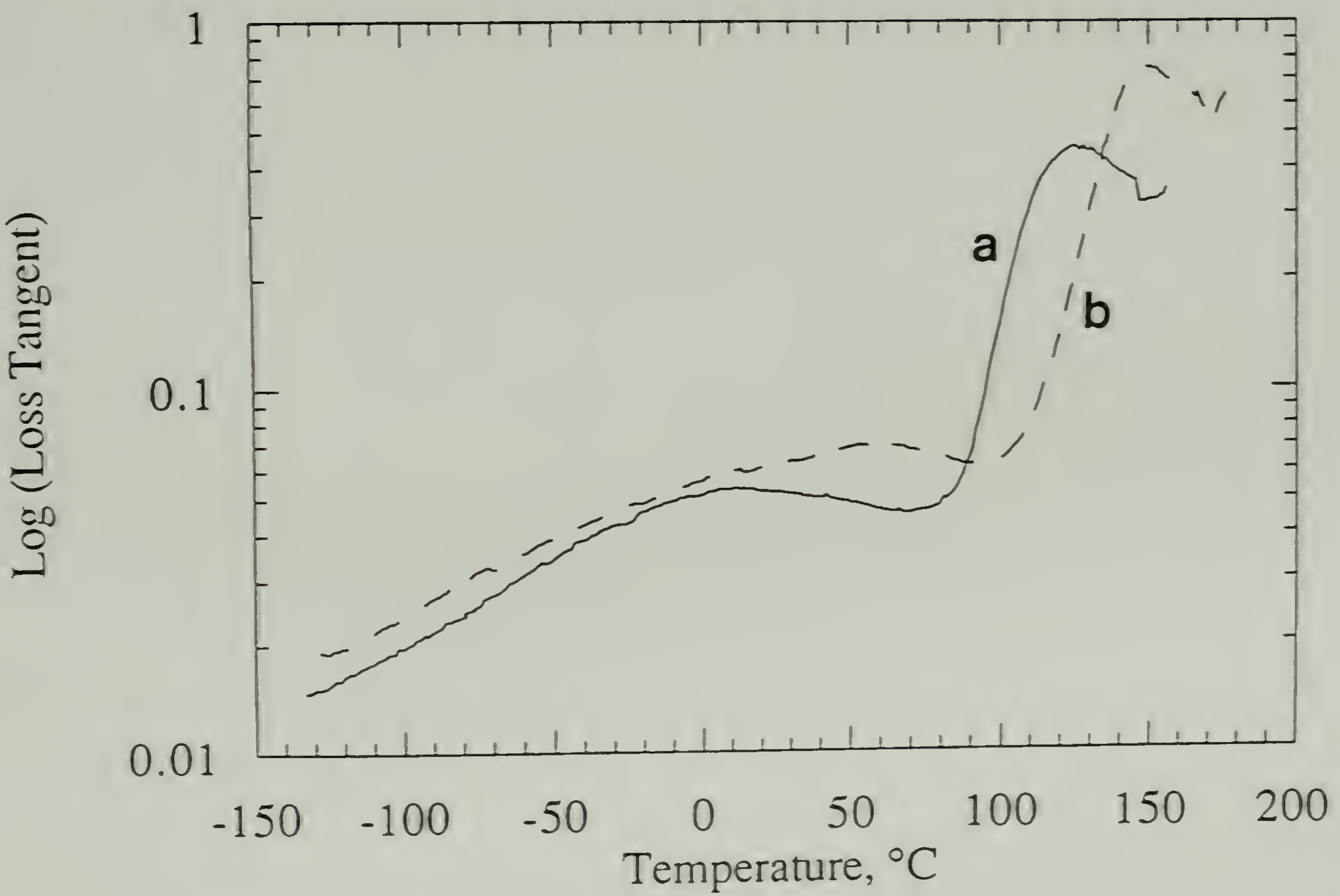


Figure 2.6. Dynamic mechanical loss tangent of slurry-chlorinated PVCs. (a) DSP-63 and (b) DSP-68. Measurement frequency is 1 Hz.

PVC results (Figure 2.4). The DSP-containing CPVC samples did not have an onset temperature greater than the unstabilized samples. PVC stabilizers are only retardants, since their action does not protect the polymer from degradative processes.

FT-IR results are similar for the slurry and solution chlorinated samples (Figure 2.7). There is a difference in the 600 to 700 cm^{-1} region of the spectrum (C-Cl stretch) for BFG-63 and CPVC-7 (these two samples have similar chlorine loadings). In the slurry-chlorinated sample, the peak at 620 cm^{-1} is split at the top. The solution-chlorinated spectrum shows a single peak at 690 cm^{-1} with a shoulder at approximately 620 cm^{-1}. The double peak centered at 620 cm^{-1} (615 and 638 cm^{-1}) is characteristic of PVC. The presence of splitting in the slurry-CPVCs may be attributable to two environments, one lightly chlorinated (PVC) and the other heavily chlorinated. Thus, structural differences between slurry and solution chlorinated PVCs can be seen by FT-IR. At higher chlorine levels, for example, BFG-68, the IR results for solution- and slurry-chlorinated PVCs are almost identical.

The microstructure of slurry-CPVCs were investigated by Komoroski *et al.*[12] and by Lehr.[13] For a given chlorine content, these materials were found to have a larger fraction of $-CCl_2-$ groups and a smaller fraction of -CHCl- groups than their solution-chlorinated counterparts. This is expected considering differences in CPVC preparation.

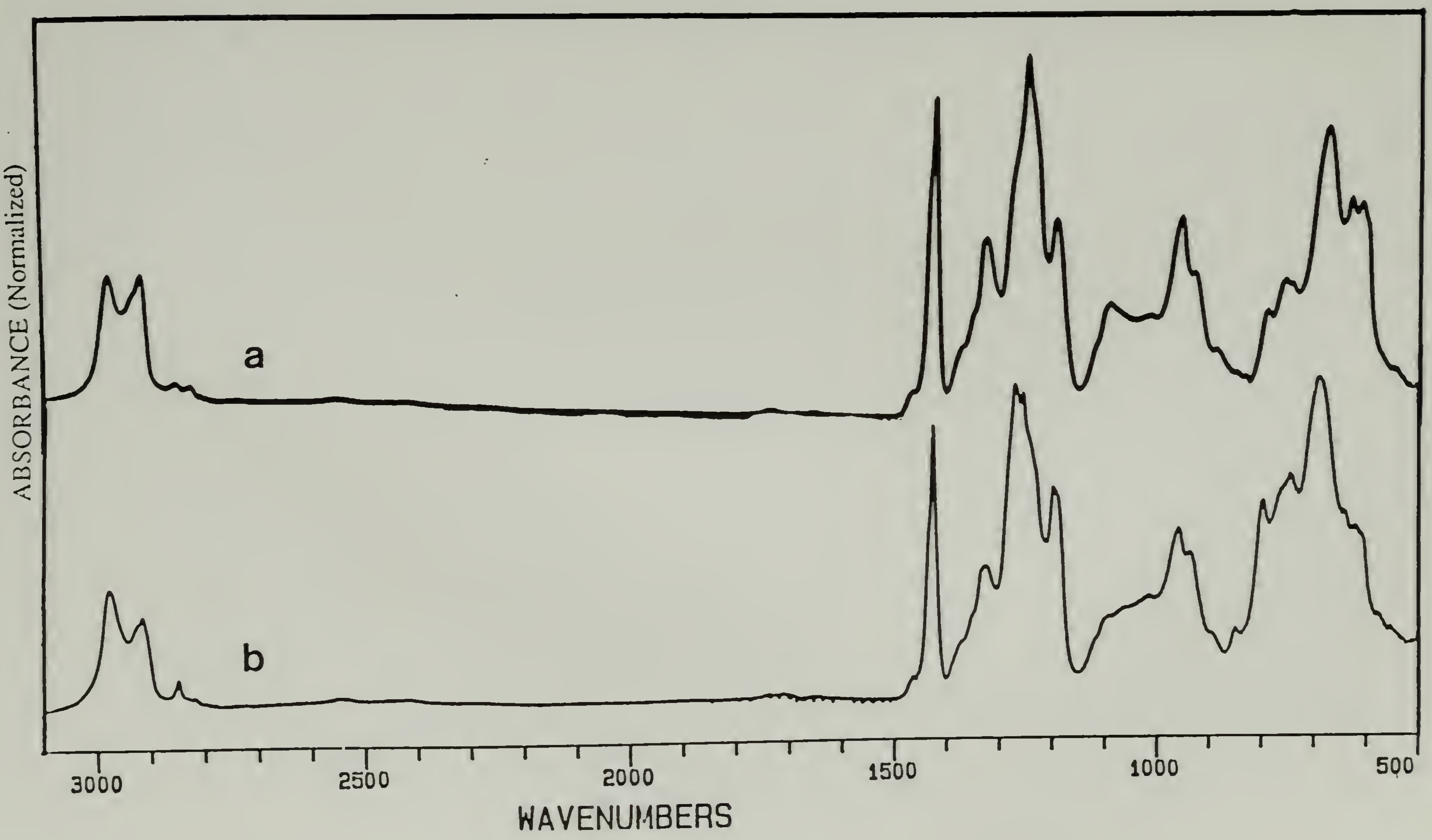
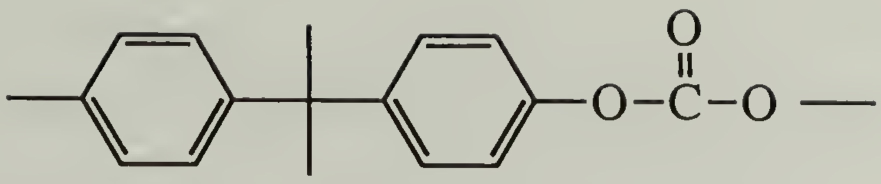


Figure 2.7. FT-IR absorption spectra of slurry-CPVCs. (a) BFG-63 and (b) BFG-68.

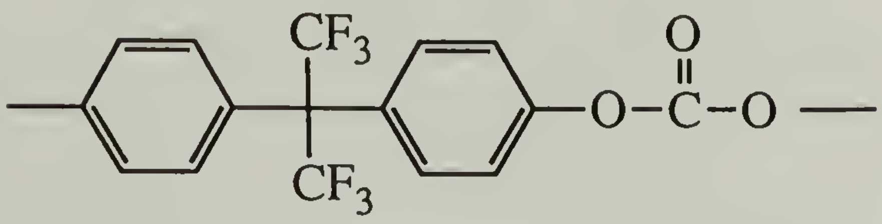
Polycarbonates

Within ten years of the commercialization of polyarylcarbonates in the 1950's, there had been a significant amount of research done on these materials. Schnell[14] and Fox and Christopher[15] described in great detail the synthesis, properties, and applications of polycarbonates. Extensive studies were done to determine the effects of phenyl ring substitution, replacement of the isopropylidene group, and copolymerization. Research is ongoing to more fully understand the properties of bisphenol-A polycarbonate and its derivatives.[16-19]

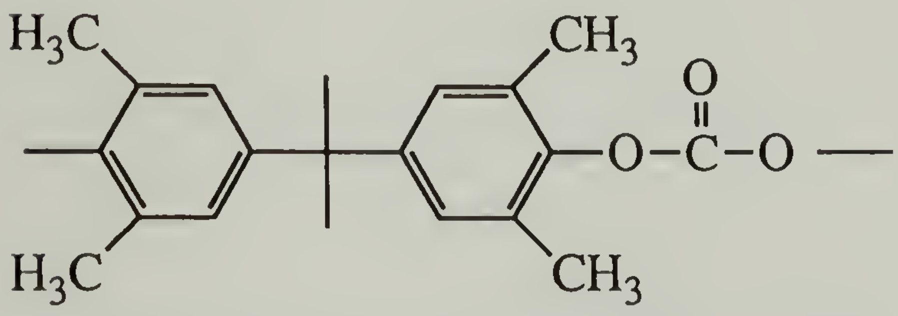
The five polycarbonate homopolymers used in this study were the polycarbonates derived from bisphenol-A (BPC), hexafluorobisphenol-A (HFPC), tetramethylbisphenol-A (TMPC), tetrachlorobisphenol-A (TCPC), and tetrabromobisphenol-A (TBPC). The repeat unit structures for these PCs are given in Figure 2.8. Molecular weight and glass transition information are summarized in Table 2.2. Molecular weights reported in the Table are relative to polystyrene standards. Relative to polycarbonate secondary standards, molecular weights are one-half the polystyrene-based values. BPC-1, BPC-2, and BPC-3 were obtained from Aldrich Chemical Company (Aldrich product no. 18,167-6). TMPC-2 was generously donated by E. E. Bostick of the General Electric Company. The remaining polycarbonates were obtained from LARK Enterprises. Materials from Aldrich and GE were used as



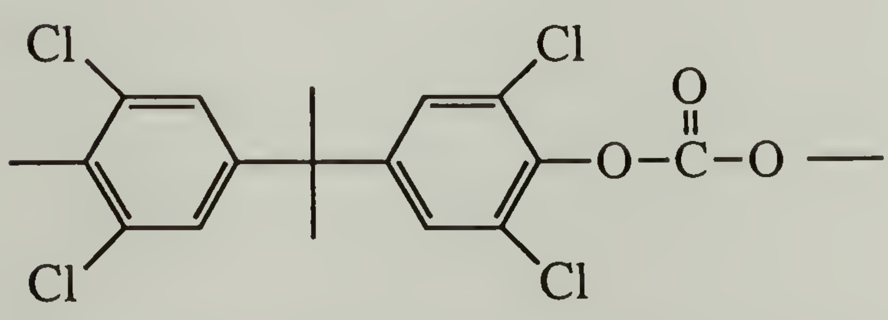
Bisphenol-A polycarbonate (BPC)



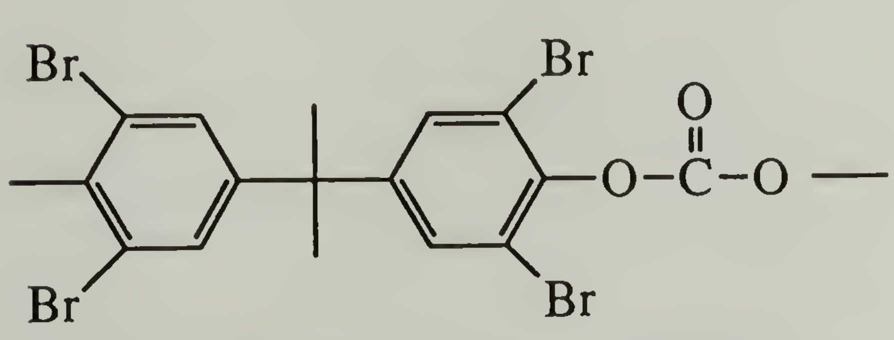
Hexafluorobisphenol-A polycarbonate (HFPC)



Tetramethylbisphenol-A polycarbonate (TMPC)



Tetrachlorobisphenol-A polycarbonate (TCPC)



Tetrabromobisphenol-A polycarbonate (TBPC)

Figure 2.8. Polycarbonate repeat unit structures.

Table 2.2. Polycarbonate characterization.

PC	$M_n (10^3)$	M_w/M_n	M_z/M_w	T_g (°C)	ΔC_p (J/gK)
Homopolymers					
BPC-0	13.1	2.63	2.01	139	0.248
BPC-1	22.4	1.90	1.55	145	0.248
BPC-2	24.9	2.14	1.57	149	0.248
BPC-3	38.0	1.98	1.59	151	0.248
TMPC-0	6.6	1.61	1.66	176	0.263
TMPC-1	25.6	2.16	1.75	197	0.263
TMPC-2	45.1	2.08	1.63	200	0.263
TCPC-0	14.2	1.96	1.59	222	0.195
TCPC-1	22.3	1.43	1.39	225	0.195
TCPC-2	41.0	1.90	1.69	226	0.195
HFPC	23.0	2.48	2.81	159	0.201
TBPC	49.6	2.04	1.66	262	0.152
Copolymers					
BPC-TCPC-25	12.3	1.96	1.94	157	0.261
BPC-TCPC-50	10.6	2.02	1.67	180	0.236
BPC-TCPC-53	57.4	2.87	1.90	200	0.195
BPC-TCPC-75	14.1	2.07	1.66	202	0.209
TMPC-TCPC-42	10.1	1.39	1.43	195	0.250
TMPC-TCPC-52	52.7	2.36	1.78	214	0.211
TMPC-TCPC-58	14.3	1.77	1.48	206	0.230
TMPC-TCPC-92	13.3	1.76	1.46	213	0.200
BPC-TBPC-50	39.0	2.03	1.59	209	0.150
HFPC-TMPC-50	9.3	1.61	1.59	161	0.215

received. All LARK samples were dissolved in methylene chloride, precipitated in an eleven-fold excess of methanol, filtered and dried in a vacuum oven prior to use.

Samples of TMPC and TCPC were fractionated by preparative GPC to determine the effect of molecular weight on glass transition temperature. The fractions had polydispersities less than 1.4. Glass transition temperature is plotted versus (1/molecular weight) in Figure 2.9. According to the Flory-Fox equation[20]

$$T_g = T_{g,o} - (K / M_n) \tag{2.1}$$

where M_n is the number-average molecular weight (with respect to polystyrene standards at 30°C; THF was the solvent), T_g and $T_{g,o}$ are the glass transition temperatures (Celsius) at M_n and at infinite molecular weight, respectively, and K is a constant. The data points are linear with K-values of $3.336 \cdot 10^5$°C for TMPC and $2.355 \cdot 10^5$°C for TCPC. At infinite molecular weight, the glass transition temperatures ($T_{g,o}$) are 202.6°C and 235.4°C for TMPC and TCPC, respectively.

As substitutions are made on the bisphenol-A unit, either at the isopropylidene group (HFPC) or at the 3,3',5,5'-phenyl positions (TMPC, TCPC, TBPC), the T_g is raised. This effect is caused by the steric hindrance of the bulky substituents on or near the normally mobile phenylene rings in BPC.[16-19] Fluorine substitution has the

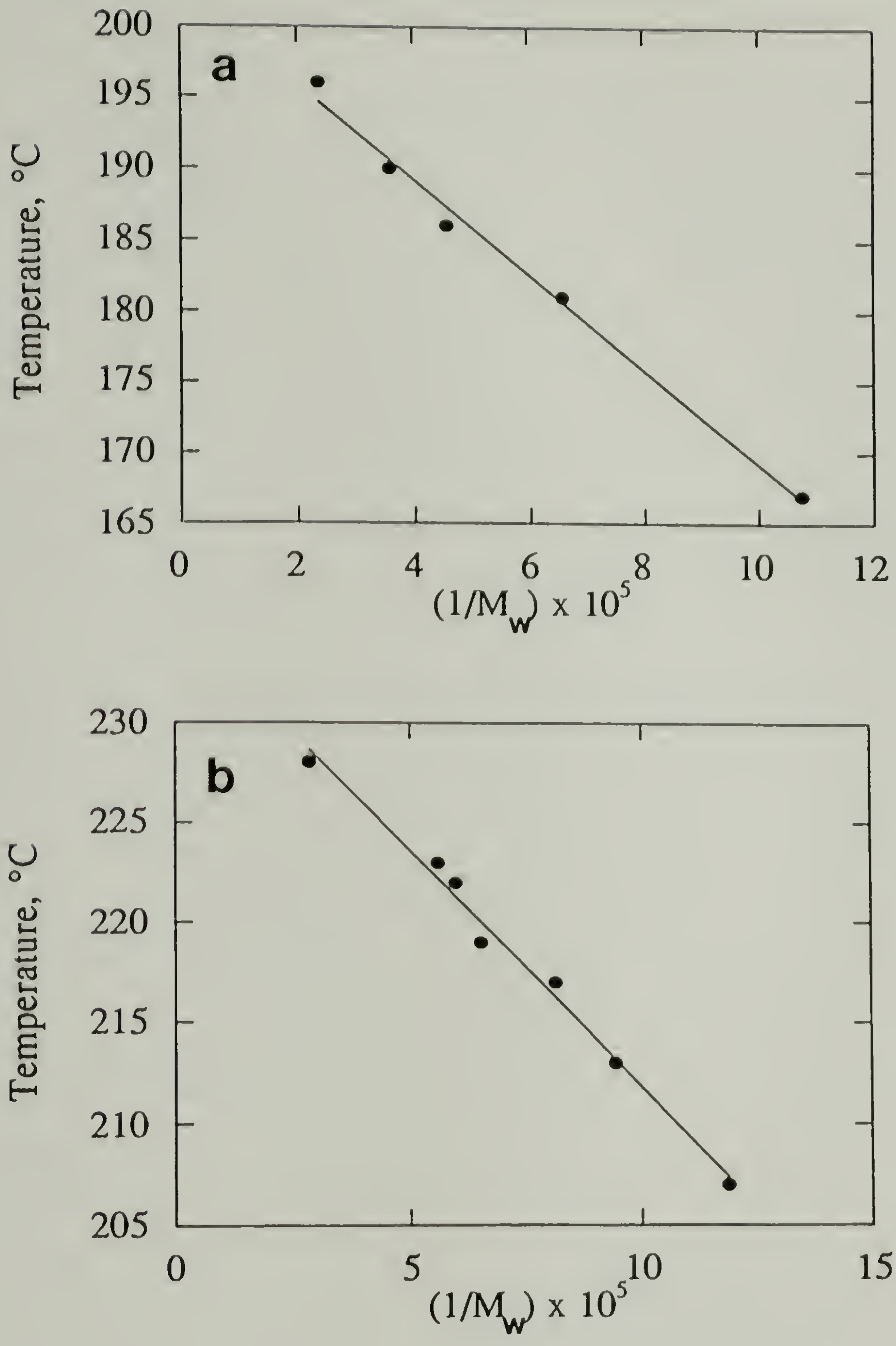


Figure 2.9. Glass transition temperatures of fractionated (a) TMPC and (b) TCPC, plotted versus inverse molecular weight.

least effect on the T_g. Literature values for HFPC range from 149°C to 170°C.[21,22] Even though fluorine substitution is on the isopropylidene group, the fluorine atoms influence the phenyl ring motions.

Only one PC, the low molecular weight BPC from LARK, showed a tendency to crystallize during precipitation from solution, and film casting from both tetrahydrofuran and methylene chloride. First heats of this BPC exhibited a melting peak in DSC at approximately 230°C. This PC could also be recrystallized from the melt. The remaining polycarbonates are amorphous solids.

Results from dynamic mechanical experiments are given in Figure 2.10. Besides having an effect on the T_g, modification is seen to affect the sub-T_g, secondary relaxations. The DMA results are in agreement with those found in the literature.[23-25]

Bulky substituents on bisphenol-A, either at the isopropylidene group or on the phenyl rings, may lead to increased polycarbonate T_g's. There have been several studies using dynamic mechanical analysis and nuclear magnetic resonance which investigate the molecular processes occurring in BPC and its derivatives.[19,23-30] Much has been deduced about the sub-T_g processes which give BPC its interesting properties. It has been determined that phenylene motion is responsible for the relaxation at -80°C in BPC. These motions are small amplitude oscillations and 180° flips about the C_1,C_4-axis. This low temperature,

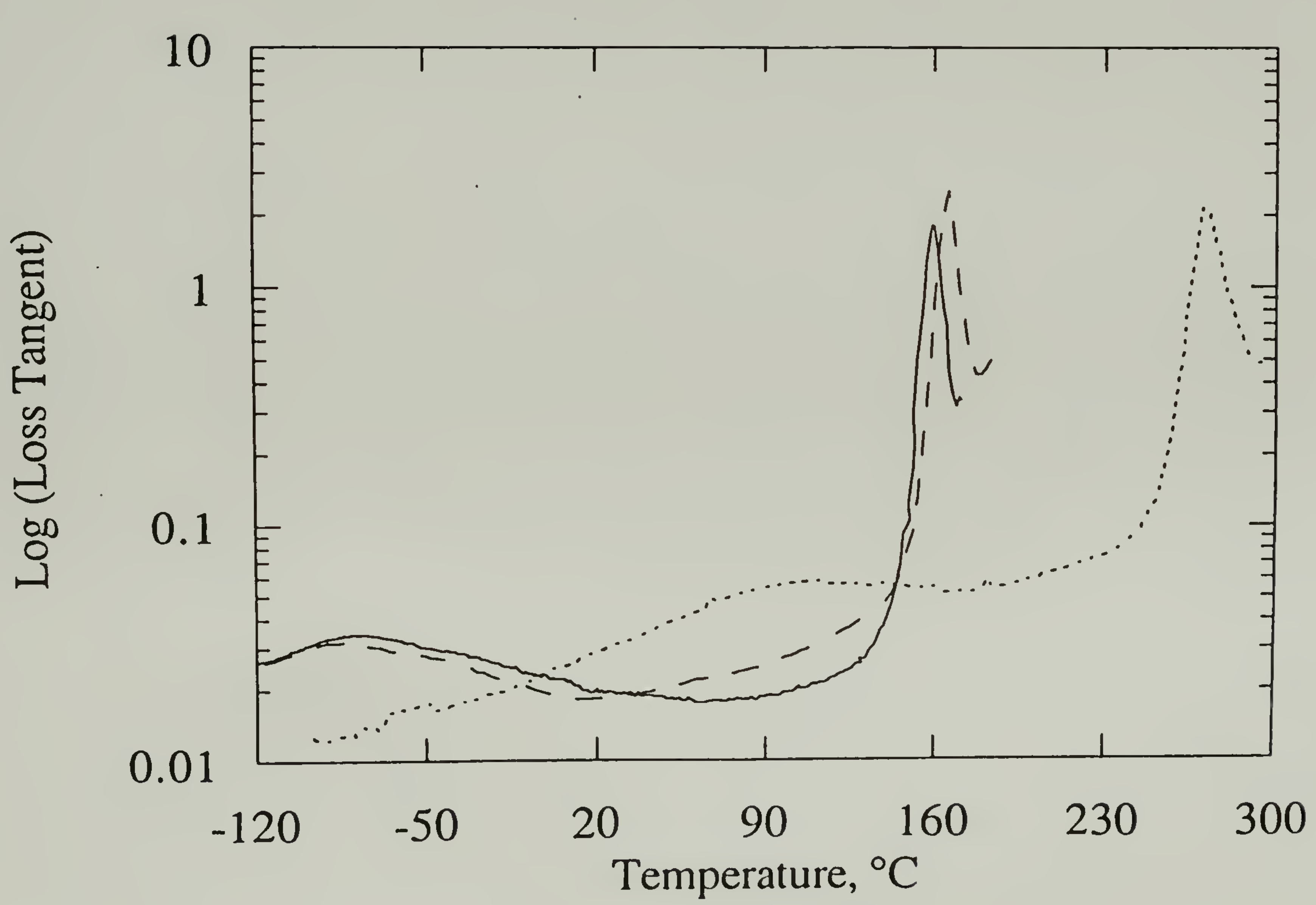


Figure 2.10. Loss tangent of BPC (solid line), HFPC (dashed line), and TBPC (dotted line). Measurement frequency is 1 Hz.

energy absorbing process is responsible for the toughness exhibited by BPC.

The effect of substitution on the glass transition temperature will depend on the location and type of group added. Yee and Smith[23] studied the effects on DMA spectra of substitution in three locations of the BPC repeat unit: replacement of the carbonyl group; substitution on the phenyl ring; and substitution on the quaternary carbon. Replacement of the carbonyl group with a methylene unit led to a 60°C reduction in the glass transition temperature, but did not affect the low temperature, *beta*-relaxation. Isopropylidene substitution affects the T_g in one of two ways. Substitution of flexible groups, such as 2,2-isobutylene, either had no effect on T_g or lowered it; bulky group substitution led to an increase in T_g. In spite of the effect on T_g, the low temperature *beta*-relaxation is not significantly affected. Substituting the aromatic protons with either halogens or methyl groups results in more complex behavior. Tetrasubstitution at the 3,3',5,5'-positions with methyl groups, chlorine, or bromine led to increases in both T_g and sub-T_g relaxations. Mono- or di-substitutions, symmetric or asymmetric, caused an increase in the sub-T_g processes. However, depending upon the substituent and its placement, the T_g increased or decreased, sometimes only slightly. Yee and Smith concluded that phenyl-ring motion is involved in all relaxation processes of PC which occur above -150°C.

Figure 2.11 shows TGA curves for three of the five PCs. Weight loss does not occur below 400^{o}C. Weight loss behavior is similar for high and low molecular weight samples. Normal processing temperatures for BPC range from 240^{o} to 340^{o}C. Above these temperatures, BPC is sensitive to various rearrangement reactions (without weight loss) and degradative processes.[31]

Of interest in the FT-IR spectra of these polymers is the carbonyl stretching vibration. If interactions exists between PCs and CPVCs, it might be expected that the carbonate linkage is involved. Shifts in the position of the C=O peak would be indicative of specific interactions with the CPVC.

The FT-IR spectra in the carbonyl region are shown in Figure 2.12. The location of this peak is sensitive to PC structure varying from 1775 cm^{-1} for BPC to 1799 cm^{-1} for TCPC. The broadened peaks of TCPC and TBPC are due to restricted conformations, frozen-in during the film-forming, solvent evaporation process. At room temperature, there is no phenylene motion so there is a distribution of environments surrounding the carbonyl. Annealing the TCPC sample at temperatures near the glass transition leads to a reduction of the high wavenumber shoulder. The FT-IR spectra for these PCs, in the 500-3500 cm^{-1} range, can be found in the Appendix.

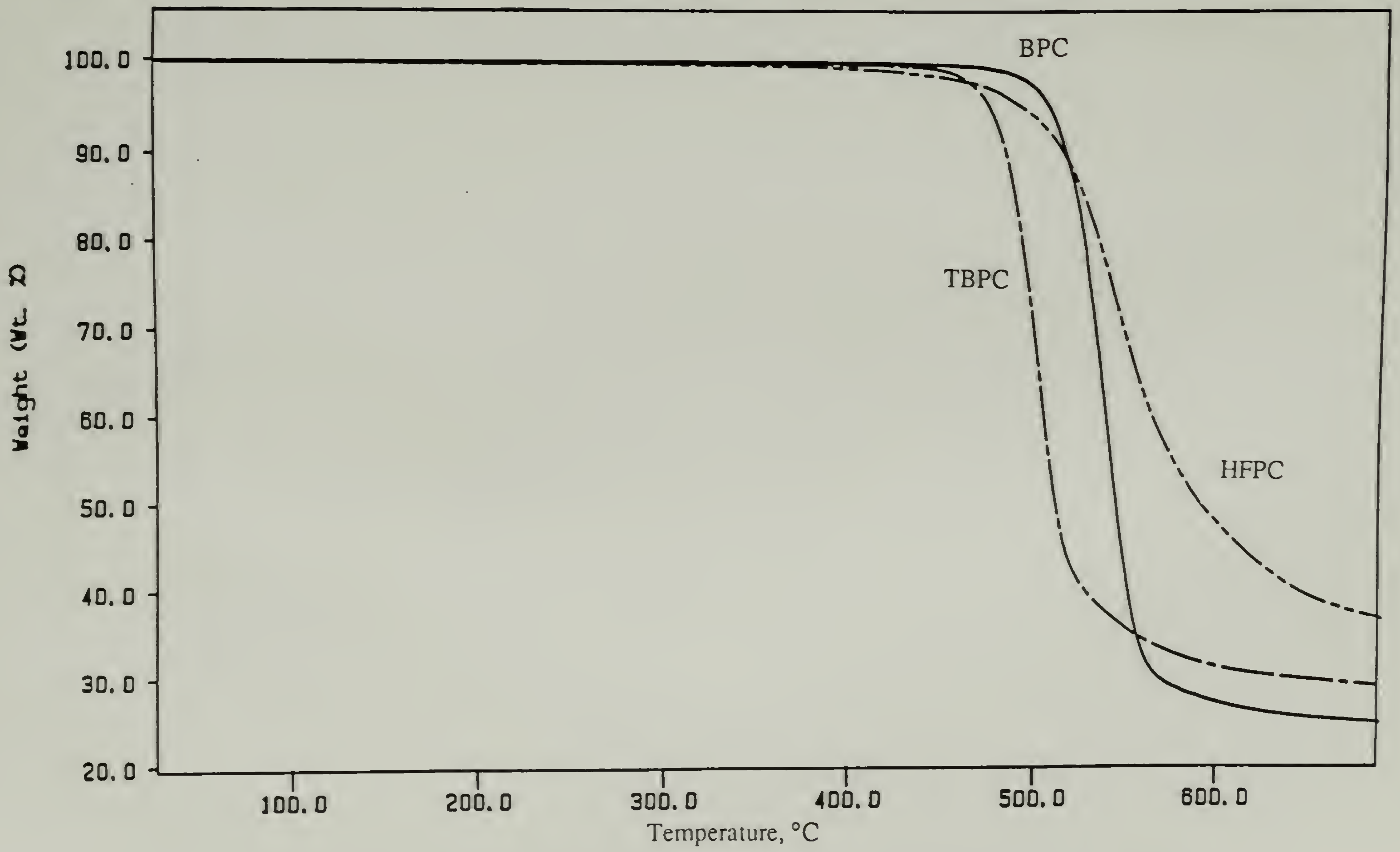


Figure 2.11. Thermogravimetric analysis of polycarbonate homopolymers.

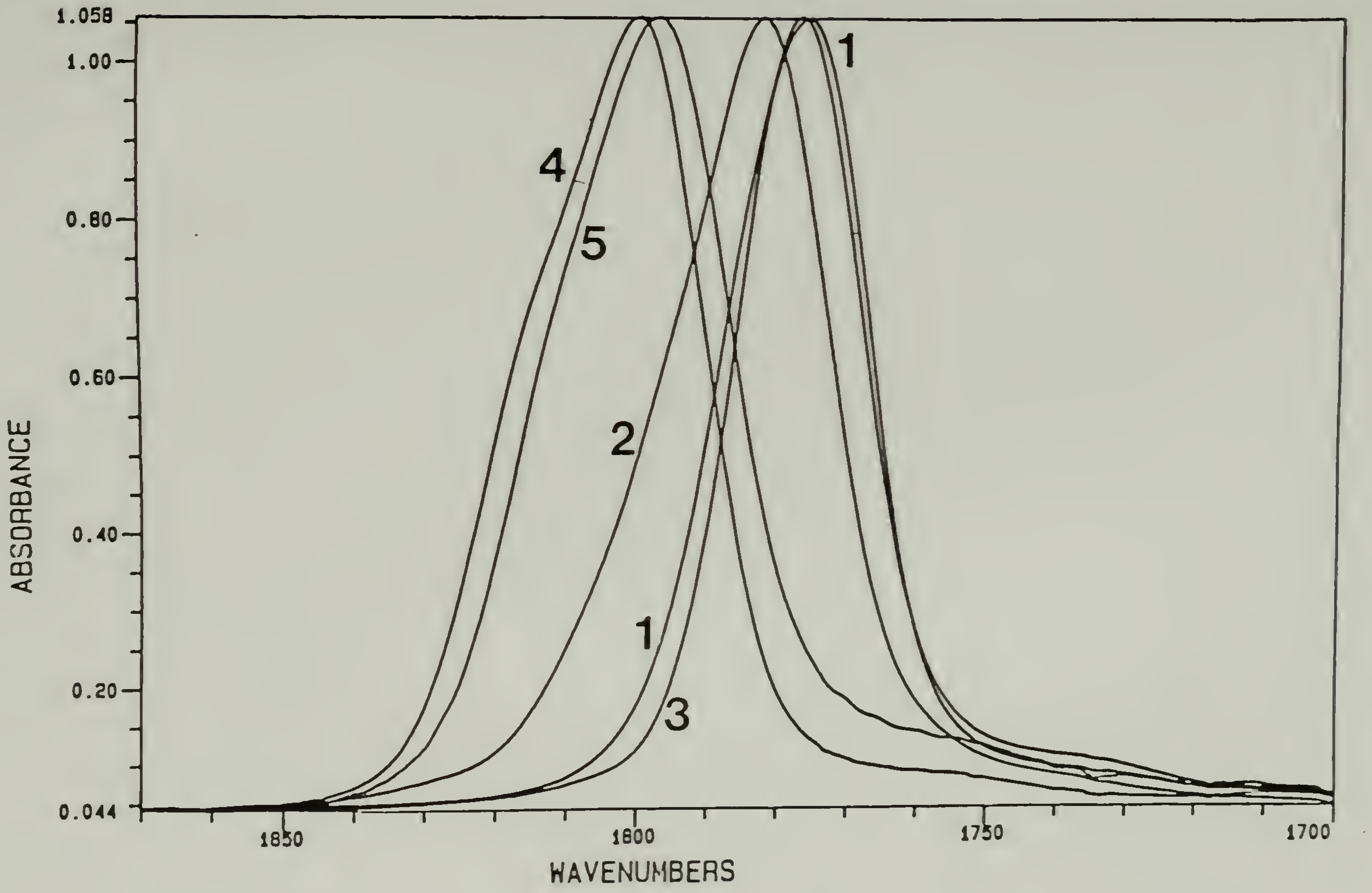


Figure 2.12. Carbonyl region of IR spectrum for the polycarbonate homopolymers. (1) BPC; (2) HFPC; (3) TMPC; (4) TCPC; (5) TBPC.

Polycarbonate Copolymers

Molecular weight and thermal characterization data from DSC for the PC copolymers used in this study are found in Table 2.2. The number designation following the copolymer identifier is the mole percent of the second component. For example, BPC-TCPC-25 is a copolymer of bisphenol-A and tetrachlorobisphenol-A having a TCPC content of 25 mole %. The compositions were determined by elemental analysis for carbon, hydrogen, and halogen (chlorine, bromine, or fluorine); this analysis was performed by the University of Massachusetts Microanalysis Laboratory.

The glass transition temperatures of the copolymers are, as expected, between the T_g's of the component homopolymers. Due to low molecular weights, some copolymers exhibit glass transition temperatures lower than homopolymers used in this investigation.

The dynamic mechanical spectra of the copolymers can provide information about the chain microstructure. Because these copolymers are of low molecular weight, one may question whether the material is truly a copolymer, or a miscible blend. DSC and DMA results confirm that these are copolymers. When annealed above 250°C, DSC measurements of low molecular weight BPC-TCPC blends reveal two glass transitions.

The DMA spectra for a 50/50 blend of BPC/TCPC is shown in Figure 2.13. This is a film sample, cast from methylene chloride and dried under vacuum at 120°C. This as-cast

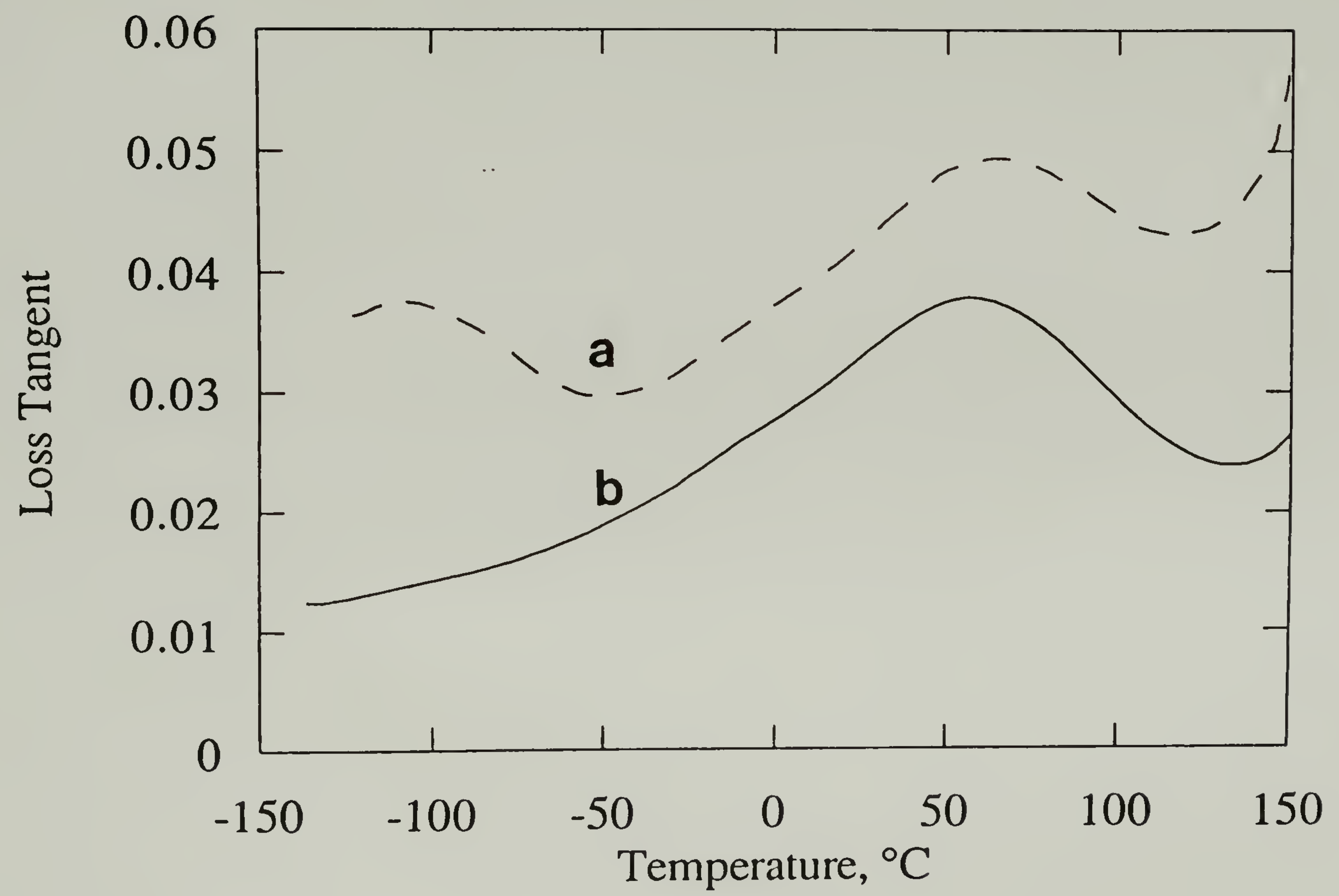


Figure 2.13. Dynamic mechanical loss tangent for (a) 50/50 (by weight) BPC/TCPC blend and (b) 50/50 (mole ratio) BPC-TCPC copolymer. Measurement frequency is 1 Hz.

sample exhibits a single glass transition at a temperature between the pure component glass transitions. Below the glass transition, the secondary relaxations for BPC and TCPC can clearly be seen. This data suggests that in the blends, the BPC and TCPC repeat units do not interact cooperatively. DMA results for a BPC-TCPC copolymer (BPC-TCPC-53) are shown in the same Figure. The secondary relaxation process for this sample is seen to be broadened and lies between the pure component transitions. In this polymer, there is cooperative interaction between BPC and TCPC repeat units because of their connectivity. These results confirm the existence of a copolymer system. Similar results have been seen in BPC/TMPC blends and BPC-TMPC copolymers.[34]

The carbonyl infrared peaks of the copolymers are broadened and located between the peak values of the parent homopolymers. In TMPC-TCPC-58, the peak is split into two peaks having peak values close to the component values. This copolymer may have a more blocky structure than the other copolymers. The size of the blocks, however, is not great enough to affect T_g behavior.

Solvent Considerations

Blend samples were prepared by codissolution in a common solvent. The polymer-polymer-solvent mixture would either be added to a non-solvent for precipitation of the polymer, or cast into glass or aluminum dishes for solvent evaporation. All solvents used were spectroscopic grade (Baker) and were used without further purification.

Tetrahydrofuran (THF) was found to be a good solvent for all the materials used in this study. This solvent was suitable for precipitation of blends, but cast samples usually contained residual THF, even after prolonged periods at 60°C under vacuum (> one week). To remove trapped solvent, temperatures above T_g were necessary which led to some discoloration of the samples (degradation of PVC and CPVC). THF is difficult to remove because it is capable of interacting with both PVC and PC.[35]

Methylene chloride was found to be a good solvent for most materials. It is known to be a solvent for polycarbonates and low molecular weight PVC. While PVC-1, PVC-2, and CPVC-1 were not soluble in methylene chloride, the remainder of the solution-CPVCs from LARK were soluble. The PVC and slurry-CPVCs from B. F. Goodrich were also soluble in methylene chloride. Use of this solvent was advantageous when casting films. Residual methylene chloride in the films was nearly zero, even under non-severe drying conditions (50°C, ambient pressure); thus many film samples were cast from methylene chloride.

Cyclohexanone was used by Braun *et al.*[36] in their investigation of BPC and TMPC blended with PVC and other chlorinated polymers (including a CPVC sample). Using the same preparation conditions described by Braun resulted in polymer degradation before solvent had evaporated. This solvent was deemed to be unsuitable, since high temperatures are necessary for cyclohexanone to evaporate.

Chloroform was also considered. While the PCs and the solution-chlorinated CPVCs (CPVC-5 and up) were soluble, the PVC samples and the slurry-chlorinated samples were not. This solvent was not used to prepare blends.

As for non-solvents, methanol was used for all polymers and their blends, except HFPC, when precipitated. Skelly-F was used to precipitate HFPC from solution during purification. The methanol was reagent grade.

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CHAPTER 3

POLYCARBONATE / POLYCARBONATE BLENDS

Application of the mean field, binary interaction model[1-3] depends upon intramolecular repulsions to drive miscibility. It is known that solution-chlorinated PVCs having chlorine contents greater than 60 % by weight are immiscible with PVC[4], and the segmental interaction parameter for vinyl chloride (VC)-1,2-dichloroethylene (DCE), the copolymer model for solution chlorinated PVC, is positive ($\chi_{VC,DCE} = 0.042$).[5] Recently, several papers have appeared in which polycarbonate/polycarbonate blend behavior has been investigated.[6-9] As has been found to be the case in many other blend studies of high molecular weight homopolymers, miscibility is found to be the exception rather than the rule.

Blends of the polycarbonates described in the previous chapter have been investigated. Three types of PC/PC blends were studied: binary blends of polycarbonate homopolymers; blends of a polycarbonate homopolymer with a polycarbonate copolymer; and polycarbonate copolymer/copolymer blends. In the nomenclature used in Chapter 1 to describe various blend systems, these may referred to as A/B, A/BC, and AB/CD systems, respectively. The mean field treatment cannot be used to estimate χ_{ij}'s from the results of A/B blends. However, these results are important for determining which PC pairs will be useful for copolymerization and blending with CPVCs. Blends which contain a PC copolymer may be used to determine PC/PC segmental interaction parameters using the mean field approach.

Experimental

Blend samples were prepared by two methods: (1) precipitation of a 4% (w/v) methylene chloride solution in an 11-fold excess of methanol; (2) film casting of methylene chloride solutions into glass or aluminum dishes. Samples were then dried in a vacuum oven until the solvent was removed (indicated by thermogravimetric analysis). The copolymers were of relatively low molecular weight (Table 2.2), so low molecular weight BPC-0, TMPC-0, and TCPC-0 were used. The similarity of molecular weights means that the critical composition will be near 50/50 by volume (by weight, if densities are similar).

Blends of varying composition were prepared for PC/PC homopolymer blends. In blends in which one component was a copolymer, 50/50 (by weight) was the primary composition studied.

Binary Polycarbonate Homopolymer Blends

Polycarbonates will be referred to by the abbreviations given in Chapter 2, Figure 2.8. Five polycarbonate homopolymers were used in this investigation. There are ten binary combinations of these PCs. Only one pair, that of BPC and TMPC, was found to be miscible in all proportions.

The T_g behavior of BPC/TMPC blends as a function of blend composition is shown in Figure 3.1. Both polycarbonates, BPC-3 and TMPC-2, are of high molecular weight. A single, composition dependent T_g is found for these mixtures, indicating miscibility. Also shown in the Figure are blend glass transition temperature curves predicted by the Fox equation[10]

$$1 / T_g = w_1 / T_{g1} + w_2 / T_{g2} \tag{3.1}$$

and the Couchman equation[11]

$$\ln T_g = (w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}) / (w_1 \Delta C_{p1} + w_2 \Delta C_{p2}) \tag{3.2}$$

where T_{gi}, w_i, and ΔC_{pi} are the glass transition temperature (Kelvin), weight fraction, and specific heat increment per unit mass (J/gK) at T_{gi}, respectively, of component i. T_g is the predicted blend glass transition temperature. BPC and TMPC are miscible at temperatures greater than 300°C.

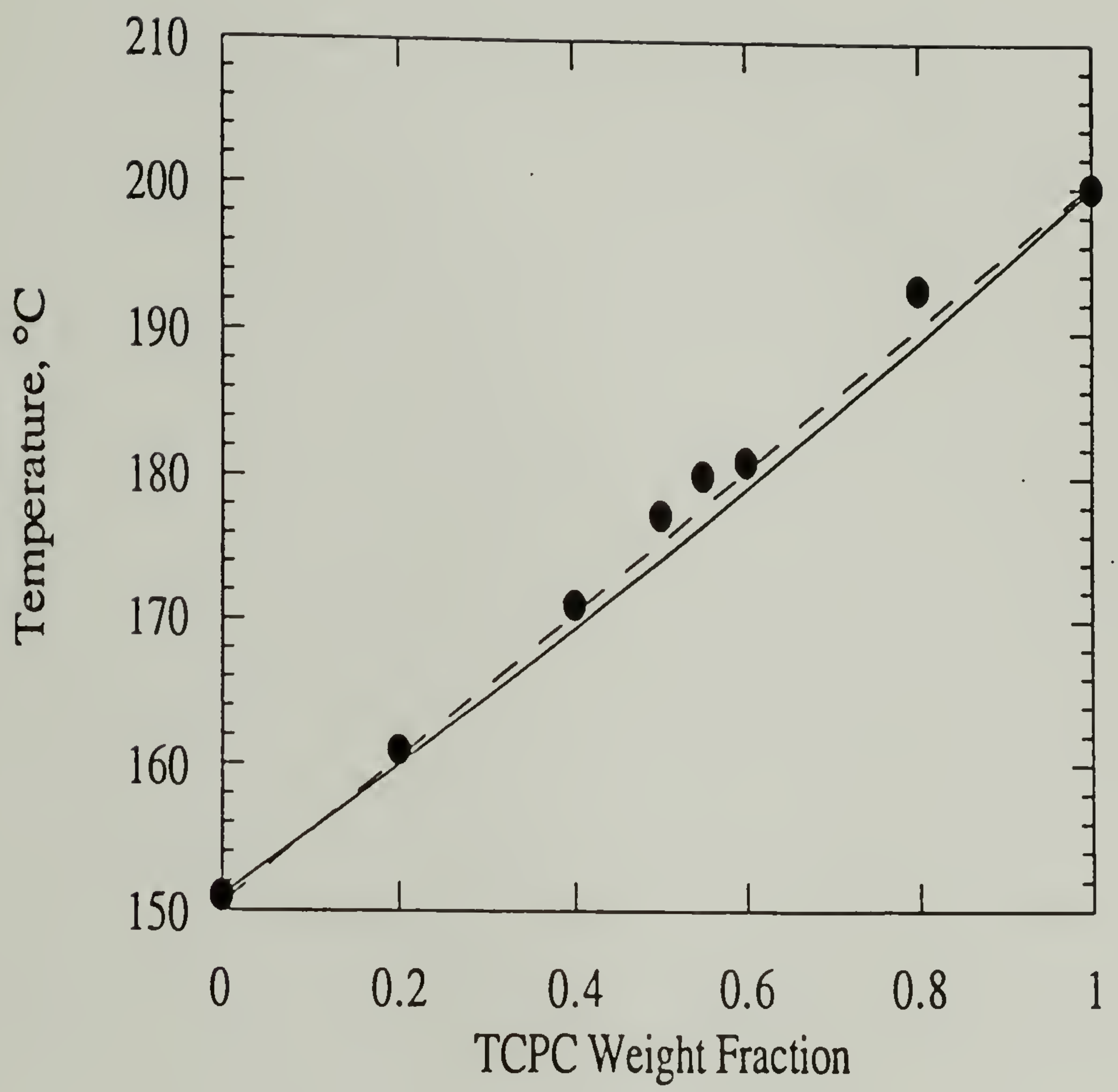

Figure 3.1. Glass transition temperature of BPC-3/TMPC-2 blends. Solid curve: predicted by Equation (3-1); dashed curve: prediction of Equation (3-2).

Dynamic mechanical analysis for this blend system both in this investigation and elsewhere[6,9] show two secondary relaxations in addition to the single, blend T_g. Each of these sub-glass transition temperature relaxations corresponds to the component secondary process. These low temperature processes are not cooperative and are evidence that a strong interaction does not exist between these two polycarbonates.

That BPC and TMPC form the only miscible pair may be explained by their similarity of structure rather than by any specific interaction. While TMPC has bulky methyl groups at the 3,3',5,5' positions which lead to the increased T_g, the interaction between BPC and TMPC repeat units is probably similar to that of BPC-BPC and TMPC-TMPC repeat unit interactions. The added methyl groups may not disturb the electron distribution in the TMPC phenyl ring, so there is little difference in the manner in which the repeat units interact with one another. Since it is unlikely that a specific interaction exists, the interaction parameter for this blend system is probably a very small positive quantity or zero.

It is worth noting that BPC and TMPC show differing behavior in their blends with poly(methyl methacrylate) (PMMA) and poly(styrene) (PS).[12-19] BPC is miscible with PMMA, but not with PS. TMPC, on the other hand, is miscible with PS and forms two-phase blends with PMMA. While the differences between BPC and TMPC may be subtle enough to allow the two polycarbonates to be miscible, it is sufficient to affect phase behavior in blends with other polymers.

Blends of BPC and TCPC were found to exhibit lower critical solution temperature (LCST) behavior. Figure 3.2 shows the glass transition temperatures of BPC/TCPC blends annealed at 270°C. Figure 3.2a is for a low molecular weight blends; Figure 3.2b is for a high molecular weight blends. The phase behavior of this polycarbonate/ polycarbonate blend system is strongly dependent upon the molecular weight of the components. As molecular weight decreases, the LCST increases, and at 270°C there are low molecular weight blend compositions which exhibit single-phase behavior. The dashed line in each of the diagrams represents the theoretical blend T_g determined by Equation (3.2). The agreement between the experimental and calculated T_g's is very good for those blends exhibiting single phase behavior.

In the high molecular weight blends, the two T_g's observed for each phase are shifted by 5° to 8°C. This shift is the same at all blend compositions. Thus, at 270°C, each phase contains some of the second component. Using Equation (3.1) or (3.2), it is possible to calculate the weight fraction of each component in the two phases. From Equation (3.1), the BPC-rich phase is found to contain 11% by weight TCPC and the TCPC-rich phase contains 8% by

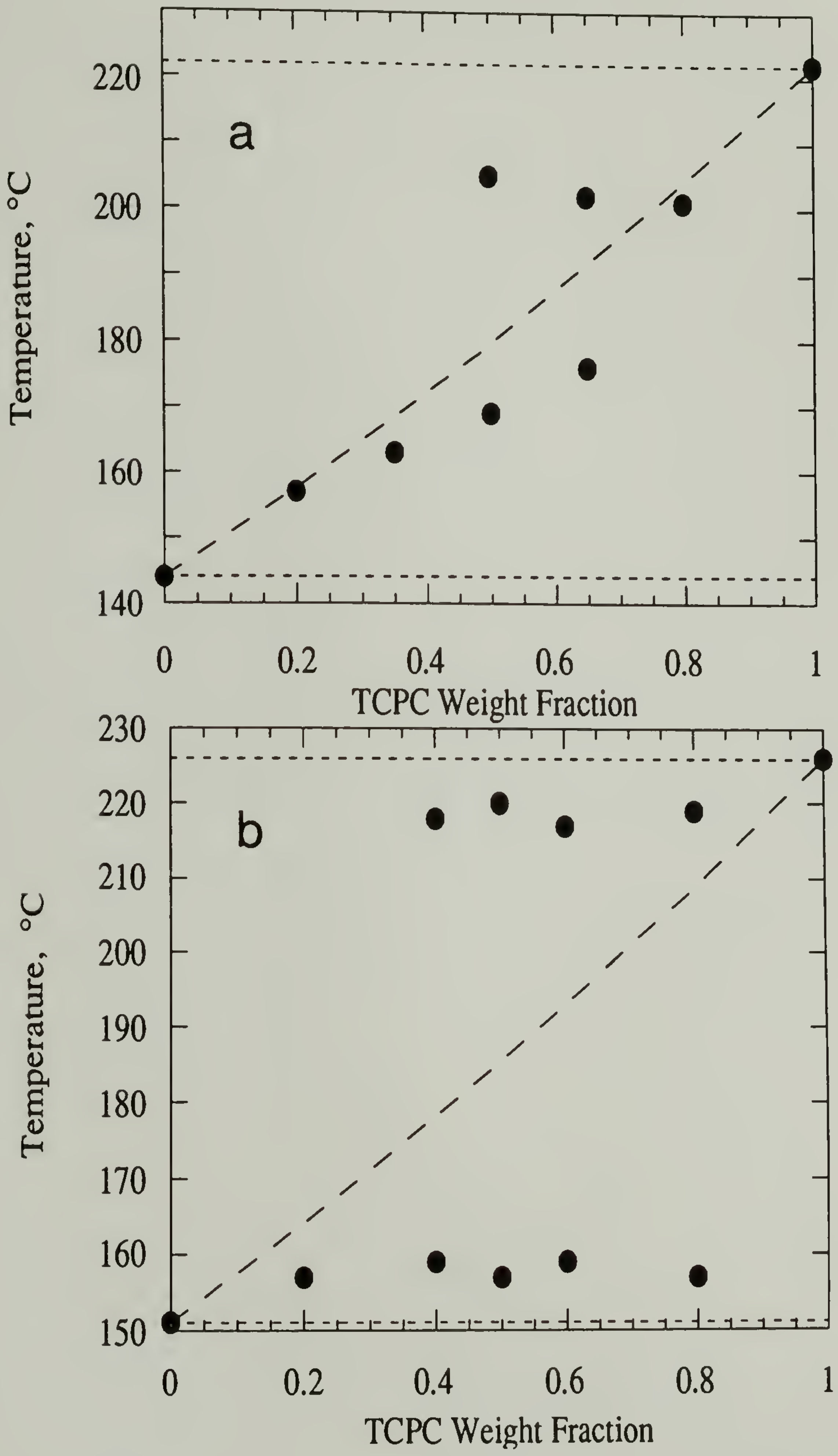

Figure 3.2. Glass transition temperatures of BPC/TCPC blends.
(a) low molecular weight blend, BPC-0/TCPC-0.
(b) high molecular weight blend, BPC-3/TCPC-2.

weight BPC. Because of the polydispersity of the polycarbonates, these values do not necessarily represent the equilibrium compositions at 270°C.[20]

Several annealing temperatures were used for each BPC-TCPC blend composition. Incremental temperature steps were 10° to 25°C. This data was used to generate a cloud point diagram for BPC-TCPC blends. Figure 3.3 shows cloud point curves for both high and low molecular weight blends. The LCST for the low molecular weight blends is between 250°C and 260°C. The critical composition, the composition at which the LCST occurs, is approximately 0.55 (weight fraction). The LCST for the high molecular weight blend is near or below the theoretical blend T_g. Determination of the LCST in these high molecular weight blends is impeded by kinetic barriers, due to the proximity to T_g.

The rise of LCST with decreasing molecular weight is predicted by Equation (1.2). As the degree of polymerization decreases, the magnitude of the contribution from the combinatorial entropy terms increases. Since these terms are always negative, reduction of molecular weight will ultimately lead to miscibility, provided the interaction parameter is small.

The TMPC/TCPC system is immiscible at all proportions at 250°C. Glass transition temperatures for TMPC/TCPC blends as a function of TCPC content are shown in Figure 3.4a. Annealing at higher temperatures shows no tendency

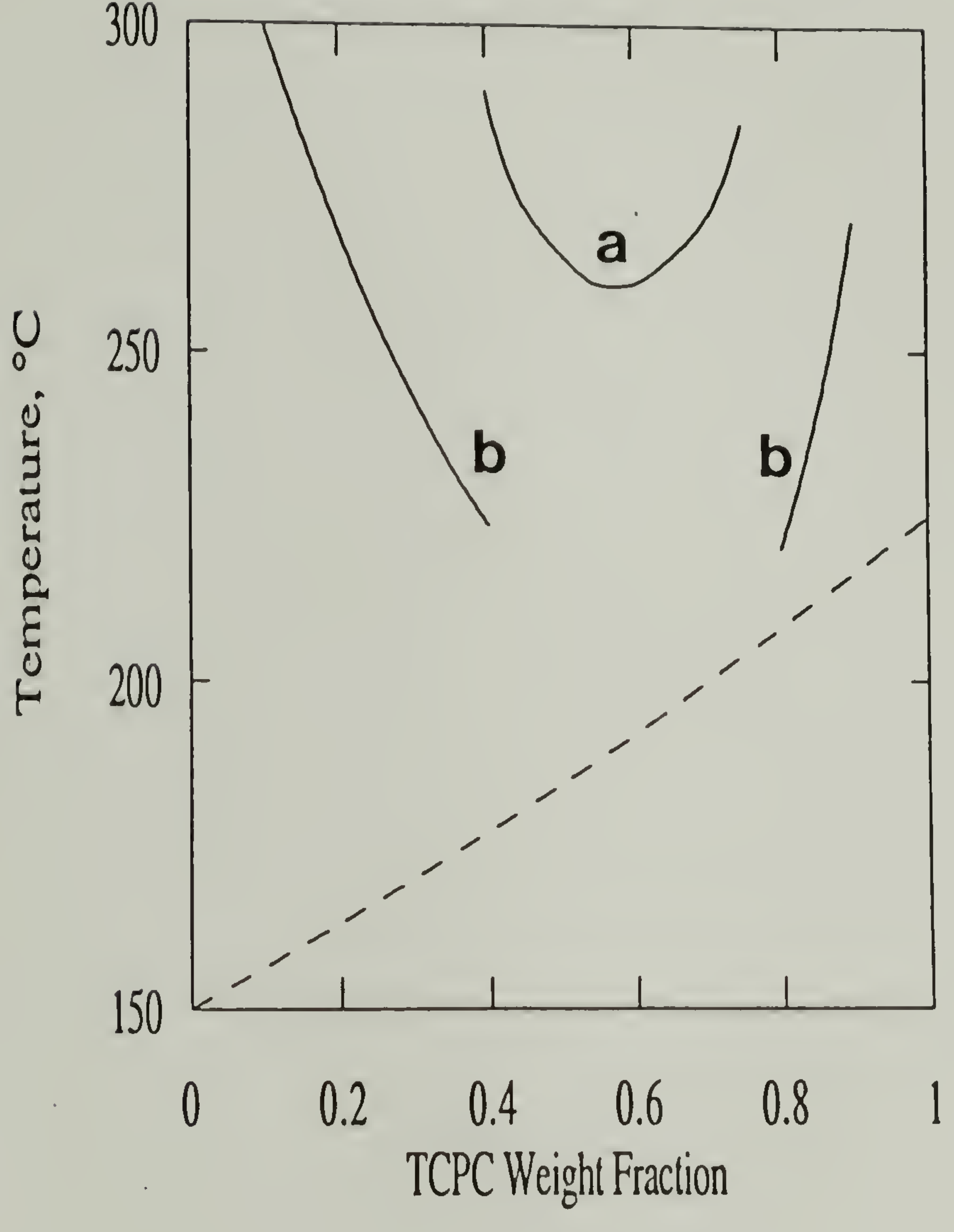

Figure 3.3. Cloud point curves for BPC/TCPC blends constructed from DSC annealing experiments. (a) low molecular weight blends; (b) high molecular weight blends.

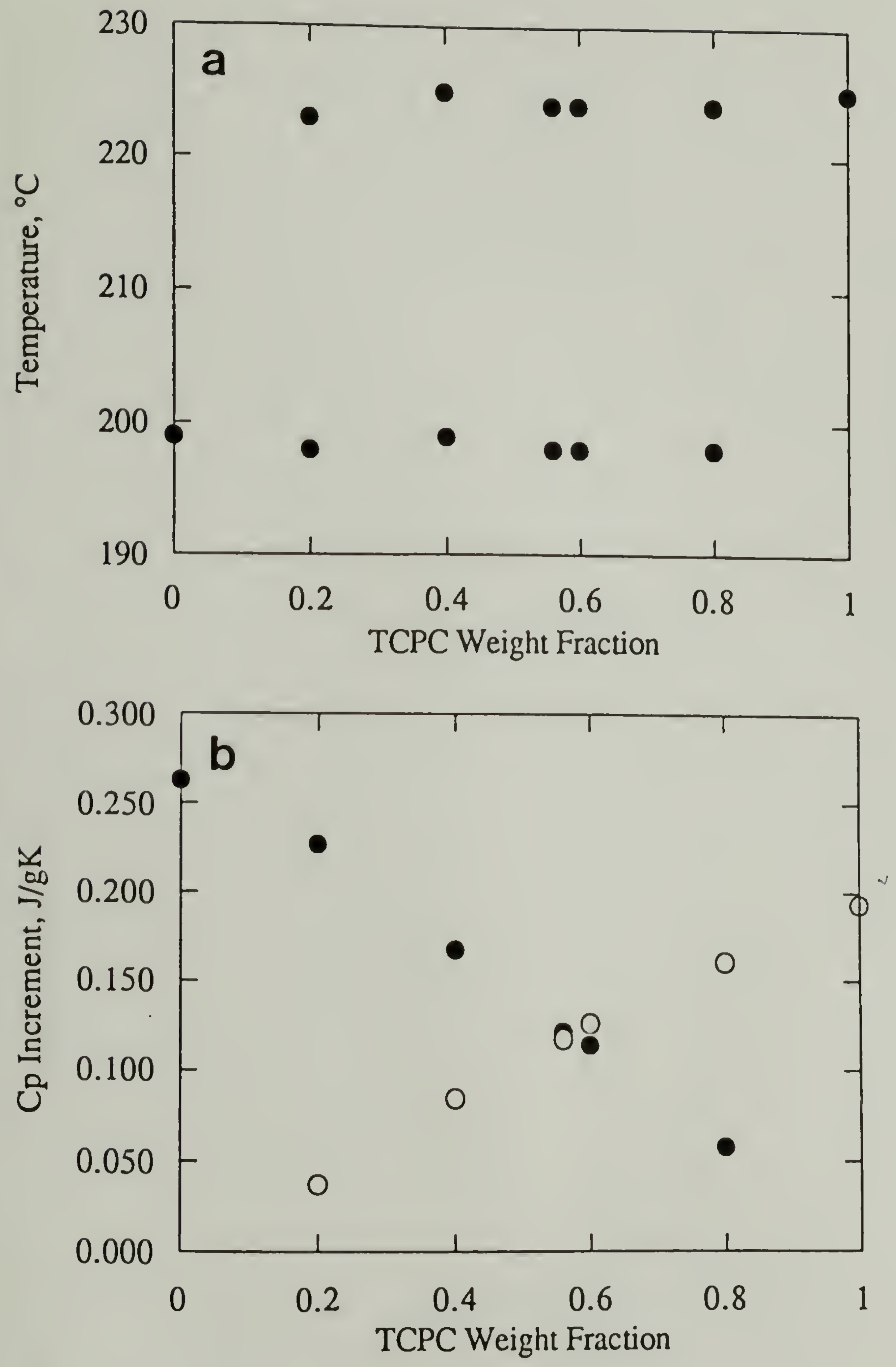

Figure 3.4. Behavior of TMPC-2/TCPC-2 blends.
(a) glass transition temperatures in blends.
(b) specific heat increment at the glass transition temperature.

for miscibility, eliminating the possibility that kinetic effects may be preventing mixing. The two T_g's seen in the phase-separated blends are identical to the pure component polymer T_g's. In addition, the incremental heat capacity change at T_g, ΔC_p, for each component approaches zero as the quantity of that component in the blend decreases (Figure 3.4b). The T_g behavior and the ΔC_p change with composition lead to the conclusion that the phases are well separated; that is, each phase is pure, and no interphase exists between the two phases. Further evidence of no mixing in either phase is gathered from the width of the glass transition as measured by DSC. The transition widths range from 8^o to 10^oC, identical to the results for the pure components. Assuming lower critical solution behavior for this system, the LSCT for this system is well below the glass transition temperatures of both TMPC and TCPC.

To determine if molecular weight would have an effect on the phase behavior of TMPC/TCPC blends, a 50/50 mixture, by weight, was prepared using TMPC-0 (M_n = 6,600) and TCPC-0 (M_n = 14,200). This blend, cast from methylene chloride, was cloudy and found to have two T_g's under the same thermal treatments as the higher molecular weight blends.

In general, as blend component T_g's approach one another, it becomes more difficult to distinguish multiple phases by DSC. In the high molecular weight TMPC/TCPC blends this difference is 26^oC. Such a value is small, yet the two phases are shown distinctly in DSC experiments. If mixed phases were present, that is, each phase having some minor component dissolved in the phase-rich component, it would be more difficult to recognize phase separation.

The phase behavior of the two blend systems discussed above provides qualitative insight into the magnitude of the segmental interaction parameters, $\chi_{BPC,TCPC}$ and $\chi_{TMPC,TCPC}$. Both interaction parameters are positive since there are blend compositions which lead to two-phase blends. The difference in magnitude between these two interaction parameters is likely to be significant. The value of $\chi_{BPC,TCPC}$ is small, being a value close to, but greater than, the $\chi_{critical}$ (Equation (1.6)) for temperatures greater than 250°C. $\chi_{critical}$ equals 0.038 for the BPC-0/TCPC-0 blend. The magnitude of $\chi_{TMPC,TCPC}$, on the other hand, may be much greater ($\chi_{TMPC,TCPC} >> \chi_{BPC,TCPC}$) since there was no composition found for which miscibility exists, even in low molecular weight blends. These arguments are qualitative, but the reasoning will be useful when the segmental interaction parameters are estimated later.

Results for the BPC/TCPC and TMPC/TCPC blend systems are confirmed by Kim and Paul.[7] In their study, 50/50 wt % blends were cast from methylene chloride solution. The cast samples were opaque and exhibited two T_g's, indicating immiscibility.

In this work, BPC/TCPC samples cast from methylene chloride were transparent, and first heats in DSC and DMA showed a single glass transition. Annealing above T_g led to phase separation of the blends. These results show the non-equilibrium state of the cast samples. This example highlights the importance of thermal history and its effect on experimental results of blend behavior.

The remaining PC/PC homopolymer blends are immiscible and experiments reveal the same trends shown by the TMPC/TCPC blends. Figure 3.5 shows DSC traces for BPC/TBPC blends annealed at 300^{o}C for 5 minutes. The other immiscible systems exhibit similar behavior. The component T_g's in the two-phase blends are identical to the pure component T_g's. When it was possible to vary molecular weight of one or both components, no change in phase behavior was observed for any of these blends. For example, BPC-1, TMPC-1, and TCPC-0 form two-phase blends with TBPC at 300^{o}C.

To summarize, only one binary combination of the polycarbonates, BPC and TMPC, formed single phase blends in all proportions at all temperatures investigated. The BPC/TCPC system is on the verge of miscibility, indicated by two mixed phases present in high molecular weight blends and miscibility in some low molecular weight blend compositions. The remaining eight combinations of PC pairs form two phase blends in which there is no sign of intermixing.

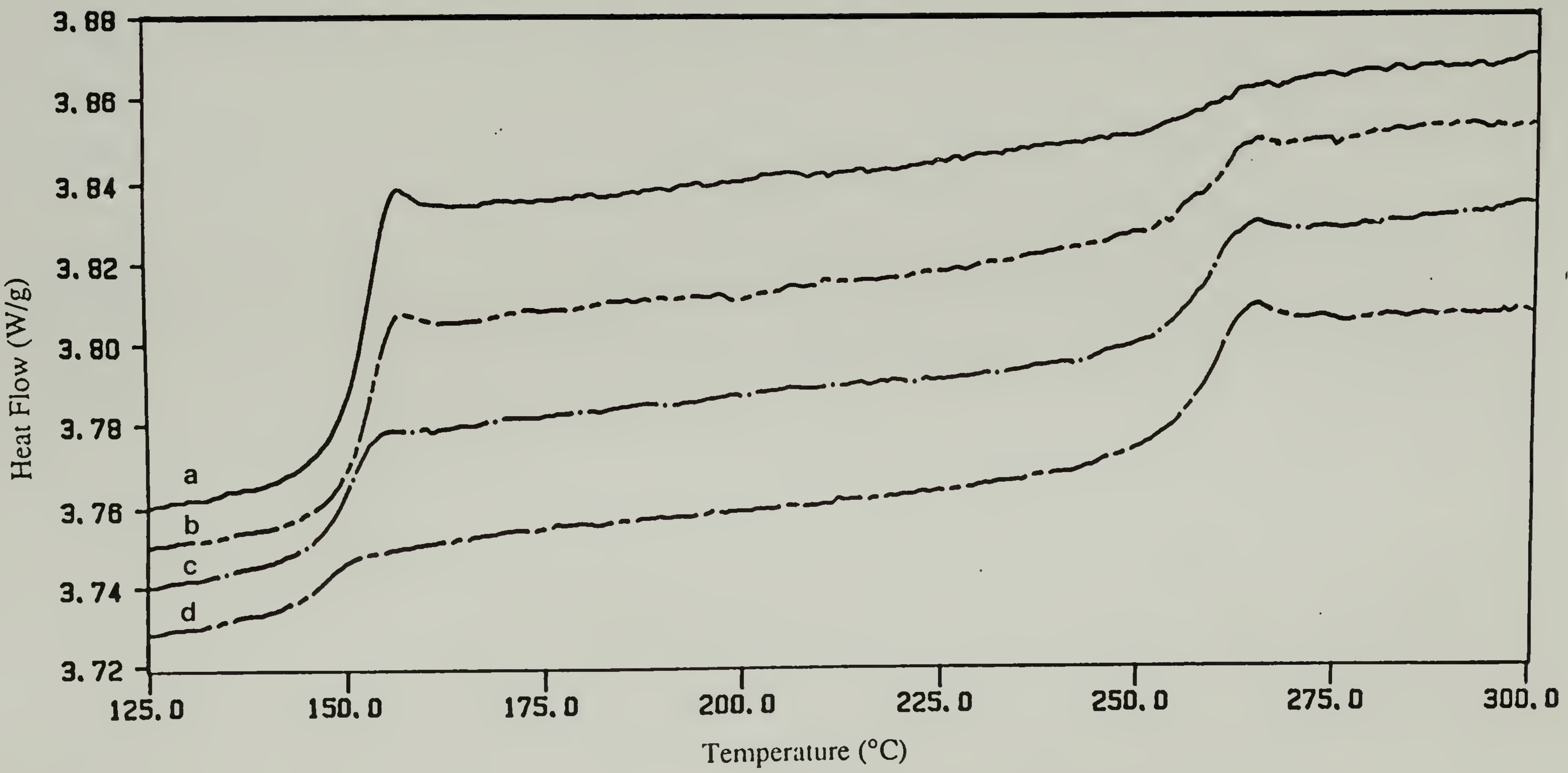

Figure 3.5. Heat capacity change with temperature for BPC-3/TBPC blends annealed at 300°C for 5 minutes. Blend composition BPC/TBPC (wt/wt): a, 80/20; b, 60/40; c, 40/60; d, 20/80.

Polycarbonate Homopolymer / Copolymer Blends ($A / B_{1-x}C_x$)

Polycarbonate blends of this type contain three segmental interaction parameters, χ_{AB}, χ_{AC}, and χ_{BC}. If binary combinations of poly(A), poly(B), and poly(C) are immiscible, there may exist some copolymer composition range, $x_1 < x < x_2$, of poly(B-co-C) which will form miscible blends with poly(A). This will depend upon the values of the segmental interaction parameters. χ_{blend} for this system, as given by the mean field treatment,[1] is

$$\chi_{blend} = (1-x)\chi_{AB} + x\chi_{AC} - x(1-x)\chi_{BC}. \tag{3.3}$$

If $\chi_{critical} = 0$ (infinite molecular weight polymers), and

$$\chi_{BC} > \chi_{AB}/x + \chi_{AC}/(1-x) \tag{3.4}$$

miscibility will result. When a miscibility window exists, it is possible to estimate segmental interaction parameters. The miscibility window has two boundaries so only two of the three χ_{ij} can be calculated. Therefore, one χ_{ij} needs to be determined independently.

If the homopolymer and copolymer share a common monomer, that is, A = B, then there is only one segmental interaction parameter, χ_{AC}, and

$$\chi_{blend} = x\chi_{AC} - x(1-x)\chi_{AC} = x^2\chi_{AC}. \tag{3.5}$$

At the copolymer composition, x, of the miscible-immiscible boundary, $\chi_{blend} = \chi_{critical}$, and χ_{AC} can be estimated. In this study $\chi_{BPC,TCPC}$ and $\chi_{TMPC,TCPC}$ were determined from blends of BPC and TCPC with BPC-TCPC copolymers, and from TMPC and TCPC blends with TMPC-TCPC copolymers, respectively.

At 265°C, all homopolymer/copolymer blends are miscible for BPC/(BPC-co-TCPC) and TCPC/(BPC-co-TCPC). Low molecular weight homopolymers BPC-0 and TCPC-0 were blended with BPC-TCPC-25, -50, and -75. Only the binary BPC-0/TCPC-0 blend was immiscible. This is an indication of the low magnitude of the positive $\chi_{BPC,TCPC}$. This data provides the information needed to calculate the interaction parameter. From the polycarbonate molecular weight data, the degrees of polymerization, N_i, are used to determine $\chi_{critical}$. Using Equation (3.5) for χ_{blend} and Equation (1.6) for $\chi_{critical}$, $\chi_{BPC,TCPC}$ was estimated. In these copolymer blend systems, the compositions of the copolymers are approximately 25 mole % apart. Therefore, the x-value corresponding to the miscibility boundary will lie somewhere in the composition range between the experimental miscible and immiscible points. This results in a range of values for $\chi_{BPC,TCPC}$. Degrees of polymerization are $N_{BPC-0} = 68$, $N_{TCPC-0} = 36$, $N_{(BPC-TCPC-25)} = 42$, and $N_{(BPC-TCPC-75)} = 41$. These values are based on weight average molecular weight, M_w, which has been shown appropriate for polydisperse materials.[21] The molecular weight is based on polycarbonate secondary standards (Aldrich bisphenol-A polycarbonate, catalog number 18,167-6). It is found that $0.041 < \chi_{BPC,TCPC} < 0.068$ at $265^{o}C$. This result is consistent with the finding of the previous section on homopolymer blends, in which it was determined that $\chi_{BPC,TCPC}$ is greater than, but close to, a value of 0.038, the $\chi_{critical}$-value.

A similar analysis was carried out on the TMPC-TCPC copolymer system. In this copolymer series, three, low molecular weight copolymer compositions were available for study, having 41, 58, and 91 mole % tetrachlorinated bisphenol-A repeat units (Table 2.2). Figure 3.6 shows DSC thermograms for TMPC-0 and TCPC-0 blended with these copolymers. These samples were annealed in the DSC at $250^{o}C$ and cooled at 320^{o}/minute prior to the scans shown. The blend proportion is 50/50 by weight. Unlike the BPC-TCPC system in which immiscibility is only realized in the binary homopolymer blend, the TMPC-TCPC copolymer system shows phase separation in blends with homopolymers well away from $x = 1$. The miscibility boundary is in the region $0.58 < x < 0.91$ for TMPC-0 and $0.041 < x < 0.058$ for TCPC-0 (x is the mole fraction of TCPC repeat units in the copolymer). $\chi_{TMPC,TCPC}$ will be greater in magnitude than $\chi_{BPC,TCPC}$. Using degrees of polymerization of 17, 36, and 33 for TMPC-0, TCPC-0, and the TMPC-TCPC copolymers, respectively, $\chi_{TMPC,TCPC}$ is determined to range from 0.167 to 0.258 at $250^{o}C$. Such a value of $\chi_{TMPC,TCPC}$ means that polymers

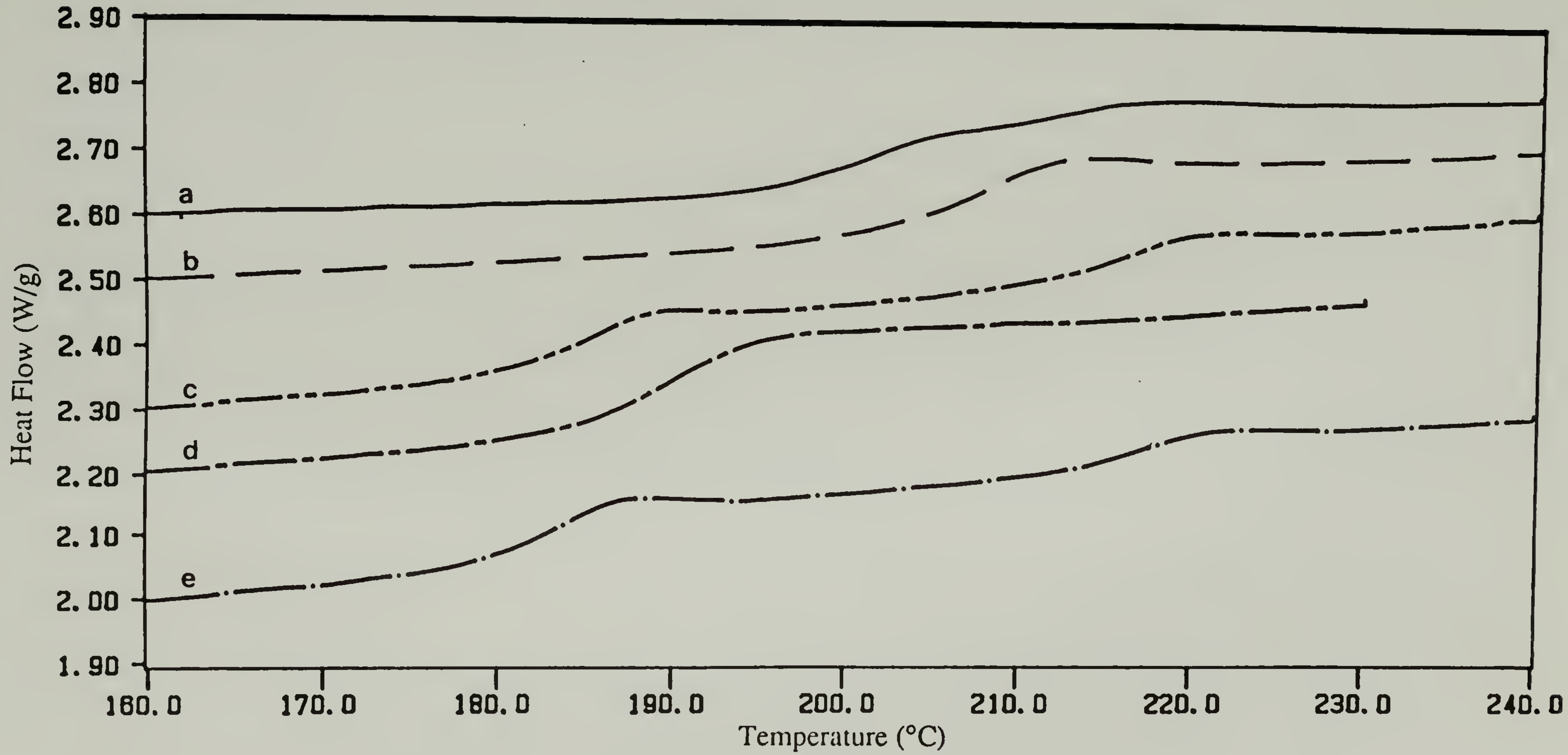

Figure 3.6. 50/50 (wt/wt) blends of TMPC-0 and TCPC-0 with low molecular weight TMPC-TCPC-copolymers. a, TCPC/TMPC-TCPC-42; b, TCPC/TMPC-TCPC-58; c, TMPC/TMPC-TCPC-91; d, TMPC/TMPC-TCPC-58; e, TMPC-0/TCPC-0. Annealing temperature and time are 200°C and 20 minutes, respectively.

having degrees of polymerization as low as eight will phase separate if blended. Again, the relative values of $\chi_{\mathrm{BPC,TCPC}}$ and $\chi_{\mathrm{TMPC,TCPC}}$ agree with the qualitative descriptions of χ_{ij} magnitude based on homopolymer blend phase behavior.

In TMPC-0/poly(TMPC-*co*-TCPC) blends, the degree of polymerization of the copolymer is nearly twice that of the TMPC. The critical concentration of this blend is not 50/50. To check if the results were affected by this, a 65/35 by weight blend of TMPC-0/TMPC-TCPC-58 was prepared. After annealing at 250°C for 20 minutes, the blend exhibited a single T_g, similar to the 50/50 blend.

Knowledge of the two interaction parameters, $\chi_{\mathrm{BPC,TCPC}}$ and $\chi_{\mathrm{TMPC,TCPC}}$, can be used to determine the interaction parameter for BPC-TMPC contacts. Blends of BPC with the TMPC-TCPC copolymers or TMPC with the BPC-TCPC copolymers ($A/B_{1-x}C_x$ blends) will have a single miscibility boundary. Since two of the three χ_{ij} are known, the unknown $\chi_{\mathrm{BPC,TMPC}}$ can be determined from Equations (3.3) and (1.6).

BPC-3/TMPC-TCPC-52 blends, in 50/50 proportion by weight, have a single T_g when annealed at 250°C and 300°C for 30 minutes. BPC blended with TMPC-TCPC-91 is immiscible after annealing under the same conditions. Calculating the degrees of polymerization from the molecular weight data in Table 2.2, it is found that $\chi_{\mathrm{BPC,TMPC}} < 0.076$ when the average values of $\chi_{\mathrm{BPC,TCPC}}$ and $\chi_{\mathrm{TMPC,TCPC}}$ are used in Equation (3.1). As the miscible-immiscible boundary varies from a TCPC mole fraction of 0.59 to 0.90, the calculated $\chi_{BPC,TMPC}$ varies from 0.076 to -0.180. More copolymer compositions within TMPC-TCPC-58 and TMPC-TCPC-91 are needed to be able to calculate a narrower range for $\chi_{BPC,TMPC}$.

Copolymers containing approximately 1:1 ratio of repeat units were available for BPC-TBPC and HFPC-TMPC. The component homopolymers are immiscible, therefore, a desirable intramolecular effect is present which will favor mixing. An estimate of the segmental interaction parameters can be determined in the same manner used above. Because of the use of only one copolymer, however, the estimated range for χ_{ij} will be large.

Second DSC traces are shown in Figure 3.7 for the homopolymers BPC-3 and TBPC blended with BPC-TBPC-50. The annealing temperature is 250°C and the samples were held at this temperature for 20 minutes. The cast films were transparent at room temperature. Inspection of BPC-3/(BPC-TBPC-50) samples after DSC testing revealed that the samples became opaque, an indication of phase separation. This separation occurred during the annealing treatment.

TBPC is miscible with BPC-TBPC-50, as indicated by a single T_g for the blend. At 250°C, there may be kinetic factors effecting mixing behavior, that is, because the T_g of TBPC is 10°C higher than the annealing temperature, phase separation may not proceed at a sufficient rate to lead to a two-phase system within the experimental time frame. This

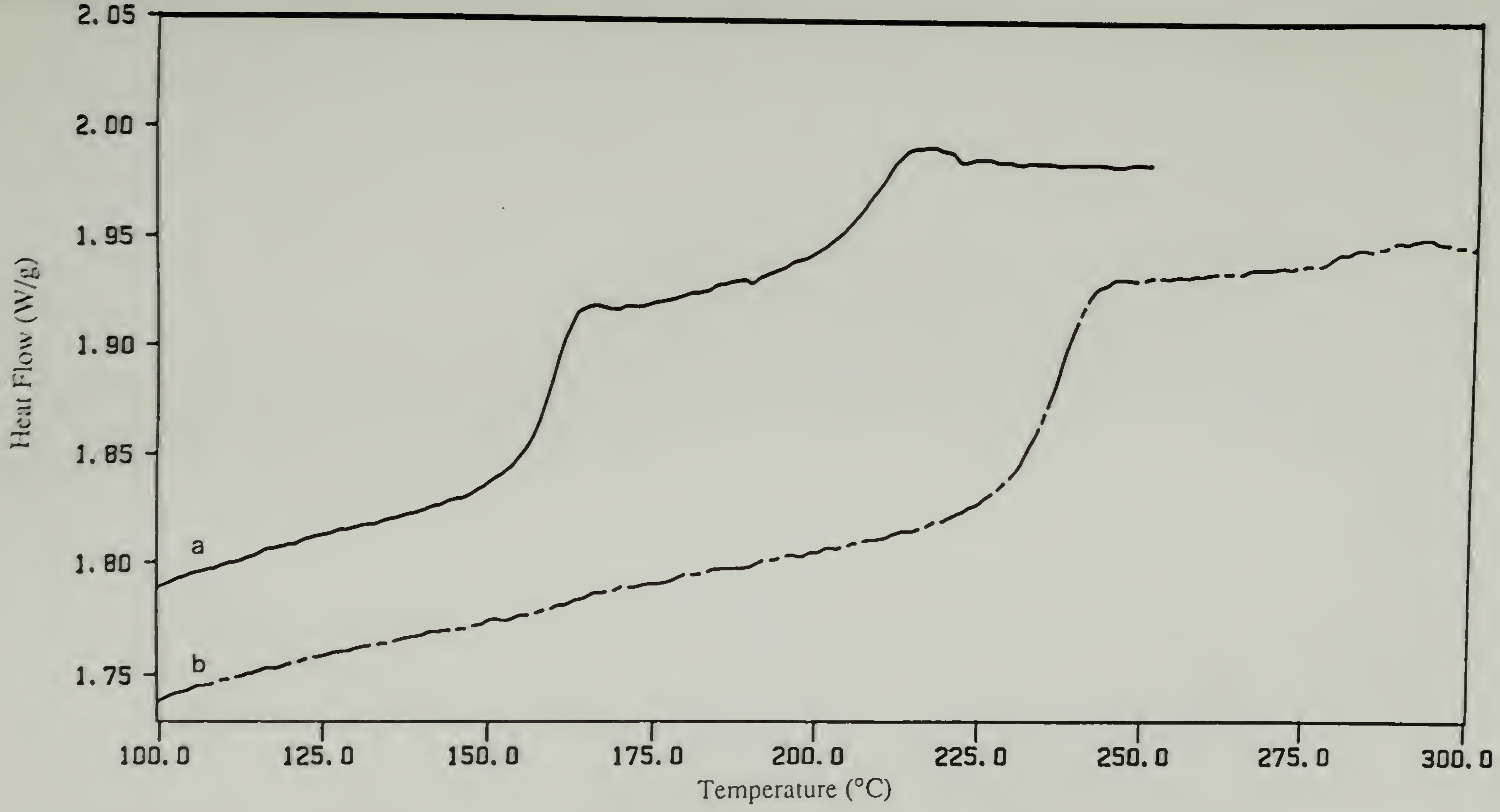

Figure 3.7. DSC thermograms of BPC-3 and TBPC blended with BPC-TBPC-50. Blends are 50/50 by weight. a, BPC/BPC-TBPC-50; b, TBPC/BPC-TBPC-50. Annealing temperature and time are 250°C and 20 minutes, respectively.

blend was also annealed at 300°C for 20 minutes; the results are similar to those at 250°C.

The difference in phase behavior between BPC and TBPC homopolymers with BPC-TBPC-50 can be understood on the basis of molecular weight. The degrees of polymerization, based on M_w, are $N_{BPC} = 148$, $N_{TBPC} = 89$, and $N_{BPC\text{-}TBPC\text{-}50} = 96$. TBPC and the copolymer have similar chain lengths. The degree of polymerization of BPC is much greater than that of the copolymer. In terms of the segmental interaction parameter, $\chi_{critical} > \chi_{BPC,TBPC}$ in the TBPC/(BPC-TBPC-50) blend and $\chi_{critical} < \chi_{BPC,TBPC}$ for the BPC/(BPC-TBPC-50) blend.

This difference in behavior is advantageous for determining the value of $\chi_{BPC,TBPC}$ because it will lead to a narrow range of values for the interaction parameter. $\chi_{critical}$ for the BPC/(BPC-TBPC-50) is 0.017 and $\chi_{critical} = 0.022$ for the TBPC-containing blend. Using $x = 0.50$ and Equation (3.5), $0.068 < \chi_{BPC,TBPC} < 0.088$.

Blends of HFPC and TMPC with HFPC-TMPC-50 are difficult to analyze by DSC. The glass transition temperatures of HFPC and the copolymer are within 2°C of one another. This is due to the low molecular weight of the copolymer. Blends with low molecular weight TMPC ($T_g = 181°C$, $M_n = 5,400$, $M_w = 7,590$) form clear films and exhibit a single T_g by DSC after annealing at 250°C and 300°C for 20 minutes. The chain lengths of these polymers are $N_{TMPC} = 24$ and $N_{HFPC\text{-}TMPC\text{-}50} =$

23. Using Equation (3.5), and taking the miscible-immiscible boundary to lie between $0.5 < x < 1.0$, $\chi_{\mathrm{HFPC,TMPC}}$ is in the range of 0.084 to 0.340.

Summary

The phase behavior of several binary, polycarbonate homopolymer blends was investigated by thermal analysis. Only one pair of polycarbonates, BPC/TMPC, was found to be miscible in all proportions, to temperatures greater than 300°C. The phase behavior of BPC/TCPC was found to depend strongly on molecular weight, and an LCST was exhibited in low molecular weight blends. The eight other binary blends were immiscible in all proportions.

Copolymer-containing polycarbonate blends were studied. From their phase behavior, it was possible to estimate segmental interaction parameters for several aromatic polycarbonate pairs. χ_{ij}'s calculated using the mean field approach are consistent with the results of binary homopolymer blend studies.

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CHAPTER 4

BLENDS OF POLYCARBONATE HOMOPOLYMERS WITH PVC AND CHLORINATED PVC

The effect of chemical modification of a polymer, and its effect on blend behavior, is an active research area. It is common practice to add functional groups which may form specific interactions and affect miscibility. In this work, the effect of modification of the bisphenol-A repeat unit--by substitution on the phenyl rings and the isopropylidene group--was investigated in blends with PVC and CPVCs. Chlorination of PVC has been shown to influence blend behavior with other polymers.[1] Previous investigations of polycarbonates (BPC, TMPC, TCPC, and TBPC) blended with PVC and/or CPVCs were reviewed in Chapter 1. It has been inferred, from results using CPVCs and other chlorinated polymers, that increased chlorination leads to miscibility with PCs. Examination of a series of solution-chlorinated PVCs blended with polycarbonates has not been undertaken.

The premise that halogenated polymers are miscible with polycarbonates is an interesting one. The conclusions of

Braun *et al.*[2] and Woo and Paul[3], which suggest that miscibility of BPC and TMPC (Braun) with vinyl chloride polymers is enhanced as the chlorine level increases, are based on a limited quantity of data. In these studies, vinyl chloride-vinylidene chloride copolymers ($-CH_2-CHCl-/-CH_2-CCl_2-$) were used to represent highly chlorinated systems. These copolymers are significantly different from CPVCs, displaying glass transition temperatures at or below room temperature. It has been shown in this work and elsewhere[4] that the glass transition temperature of a CPVC increases as the chlorination level is increased. The chlorine distribution within the polymer is a significant factor effecting physical properties[5] and interactions with other materials.

Blends of polycarbonate homopolymers with PVC are of the A/B-type (poly(A) blended with poly(B)). While these blend systems cannot be used for the estimation of segmental interaction parameters using the mean field approach,[6-8] the identification of polycarbonates miscible with PVC is nonetheless important. These materials may prove useful as modifiers for PVC.[9-13]

PCs blended with solution-CPVCs are $A/(B_{1-x}C_x)$-type blends, where x is the fractional composition of monomer C in the copolymer. Solution-CPVCs are modeled as a vinyl chloride-1,2-dichloroethylene copolymer. Phase behavior in these blends depends upon three interaction parameters. The objective of this section is to present the results of the investigation of polycarbonate homopolymers blended with PVC and a series of solution-CPVCs having incrementally increasing chlorine content. In addition to the solution-CPVCs, slurry-CPVCs were blended with the PCs to determine what, if any, effect chlorine distribution in the CPVCs might have.

Experimental

Preparation of PVC-containing blends depended upon the PVC used. PVC-0 was soluble in methylene chloride, a good solvent for PCs, and blends were cast into thin films from methylene chloride solution (4% w/v). PVC-1 and PVC-2 were insoluble in methylene chloride but soluble in THF (tetrahydrofuran). Blends containing these PVCs were cast from THF solutions (4% w/v) to form thin films and/or precipitated in an eleven-fold excess of methanol. The precipitated samples were placed under vacuum at 60°C until dry (determined by thermogravimetric analysis). Films cast from methylene chloride were treated under the same drying conditions. THF-cast films, however, required higher drying temperatures to remove solvent. Under nitrogen, the temperature would be cycled to as high as 150°C. Cycling minimized exposure to degrading thermal conditions.

All CPVC-containing blends were cast as thin films from 4% w/v methylene chloride solutions. Methylene chloride was allowed to evaporate at 30°C under a nitrogen stream. Once the films formed, the temperature was raised to 50°C and, under nitrogen, the sample was left to dry. One to two days was usually sufficient to remove all traces of the solvent from the films. Thermogravimetric analysis was used to determine the residual methylene chloride content.

Unsupported films for FT-IR were prepared by solution casting. Typical thickness of these films was 0.020 mm. Thick films for dynamic mechanical analysis were prepared by solvent casting in layers, each layer being allowed to dry before addition of the next solution layer.

PVC Blended with Polycarbonate Homopolymers

The DSC behavior of three PC/PVC blend systems as a function of blend composition is summarized in Table 4.1. The PCs are BPC-3, HFPC, and TMPC-2. The poly(vinyl chloride) in the blends is PVC-0. BPC and HFPC blends were annealed at 180°C for 20 minutes; TMPC/PVC blends were annealed at 200°C for 15 minutes.

BPC-3 and TMPC-2 are immiscible with PVC, a result consistent with previously published results.[2,3] HFPC is also immiscible with PVC, despite its low molecular weight. The glass transition temperatures of each phase correspond to the pure component T_g's. In PC-rich compositions, where the incremental heat capacity change at T_g (ΔC_p) could be measured for both PC and PVC phases, the ratio of $\Delta C_{p,\text{measured}}$ to $\Delta C_{p,\text{calculated}}$ lies between 0.95 and 1.06. $\Delta C_{p,\text{calculated}}$ is the product of the pure component ΔC_p multiplied and its weight fraction, w, in the blend. Both

Table 4.1. Results from DSC experiments for blends of PVC with polycarbonate homopolymers.

Blend	Weight Proportion	Glass Transition Temperature, °C
BPC-3 / PVC-0	20 / 80	76 / -
	40 / 60	77 / 148
	60 / 40	77 / 149
	80 / 20	77 / 150
TMPC-2 / PVC-0	20 / 80	79 / -
	35 / 65	79 / -
	50 / 50	80 / 198
	65 / 35	80 / 199
	80 / 20	80 / 200
HFPC / PVC-0	25 / 75	79 / -
	50 / 50	79 / -
	75 / 25	80 / 161

the glass transition temperatures and the ΔC_p behavior indicate a lack of mixing in these blends.[14]

Low molecular weight blends of BPC and TMPC with PVC were studied to determine the effect of chain length on miscibility. Blends of BPC-0 and PVC-0 were immiscible, and like the high molecular weight blends, there was no indication of mixing within each phase. A low molecular weight fraction of TMPC (M_n = 8,400, M_w = 11,700) blended with PVC-0 (50/50 by weight) exhibited a PVC-phase glass transition temperature of 83°C, 7°C higher than pure PVC-0. The TMPC T_g was obscured by the PVC melt endotherm. A small fraction of low molecular weight TMPC, mixed in the PVC-rich phase, is responsible for this increase in the PVC glass transition temperature.

In its blends with BPC, HFPC, and TMPC, PVC still exhibits a melt endotherm, and in PVC-rich compositions, the endotherm obscures the polycarbonate glass transition. In an attempt to better resolve the polycarbonate glass transition, a quenching study was done with BPC/PVC blends. Samples were quenched in liquid nitrogen from temperatures of 180°C to 230°C. This was accomplished by removing the sample from the DSC cell and immediately immersing the sample in liquid nitrogen. In the liquid nitrogen-cooled samples, a crystallization exotherm immediately follows the PVC glass transition (Figure 4.1). Because of PVC crystallization above its T_g, these attempts at improving polycarbonate T_g resolution were unsuccessful.

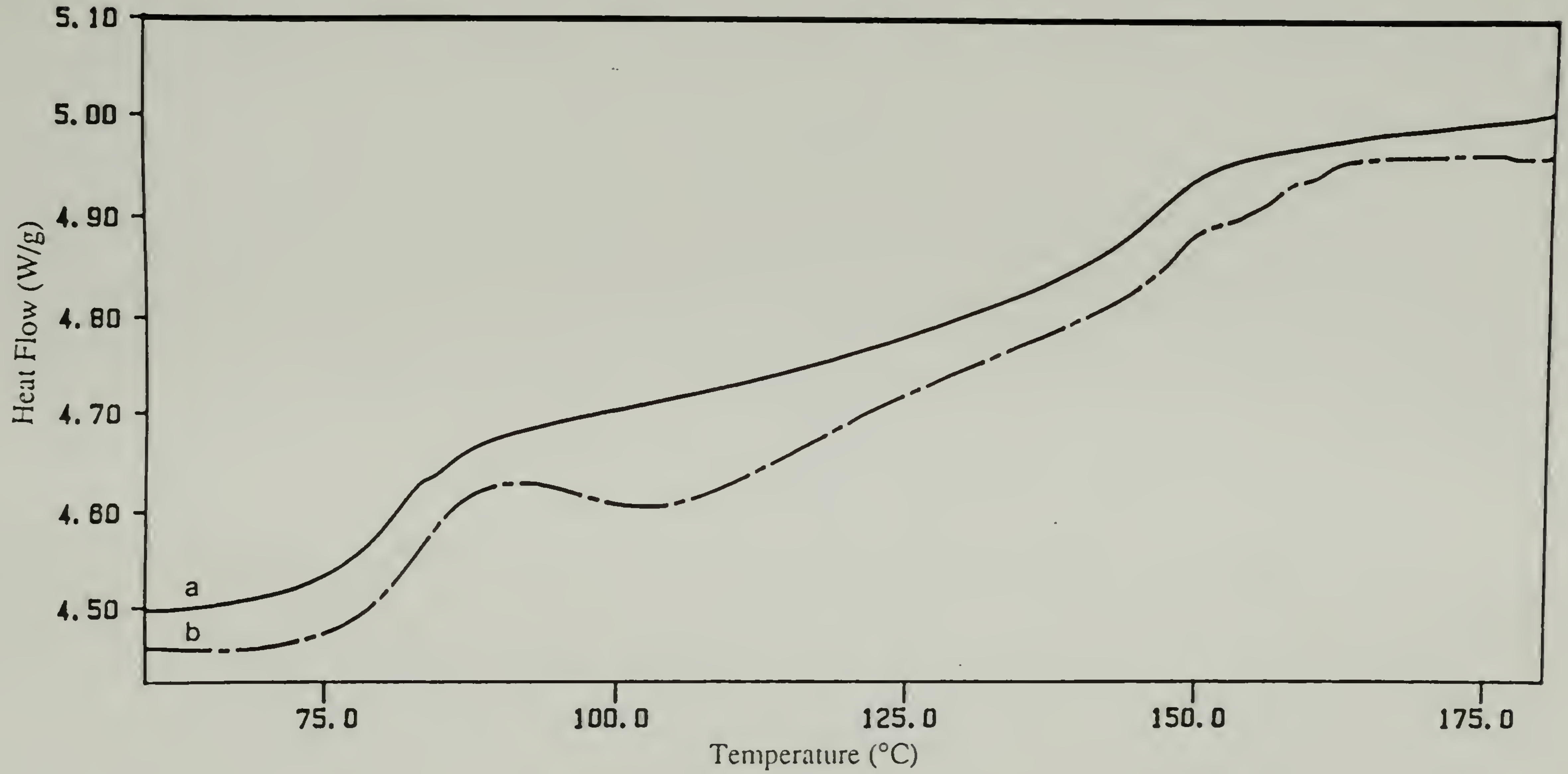

Figure 4.1. DSC behavior of BPC-1/PVC-0 blend (40/60 by weight).
a. cooled at 40°C/minute from 180°C.
b. quenched in liquid nitrogen from 180°C.

Tetrabromobisphenol-A polycarbonate (TBPC) appears to be miscible or "partially miscible" with PVC (Figure 4.2). A blend is "partially miscible" if the two T_g's of the blend are shifted toward one another, an indication of partial mixing. The measured blend T_g is sensitive to the thermal history of the sample. The glass transition temperature of TBPC is too high for a thorough investigation of its blends with PVC. Below $200^{\circ}C$, a single T_g is seen in 50/50 (by weight) blends. This transition is broad (> $15^{\circ}C$) and the measured glass transition temperature is less than the T_g predicted by either the Equation (3.1) or (3.2). For example, a miscible 50/50 blend of TBPC and PVC-1 should have a T_g near $155^{\circ}C$, as predicted by Equation (3.1). In the DSC experiments, a sample annealed at $180^{\circ}C$ for 20 minutes had a T_g of $101^{\circ}C$, a difference of $54^{\circ}C$. The breadth of the glass transition suggests that large composition fluctuations are present within the blends.

An explanation for the observed behavior in TBPC/PVC blends is a state of non-equilibrium existing in the cast films. It is desirable in blend studies to anneal at temperatures above the T_g's of the blend components. Annealing at elevated temperatures is necessary to eliminate kinetic barriers which may hinder phase separation or mixing. The high T_g of TBPC and the poor thermal stability of PVC make it impossible to anneal at the proper temperatures to reach thermodynamic equilibrium. The $180^{\circ}C$ annealing temperature is only $25^{\circ}C$ above the predicted blend

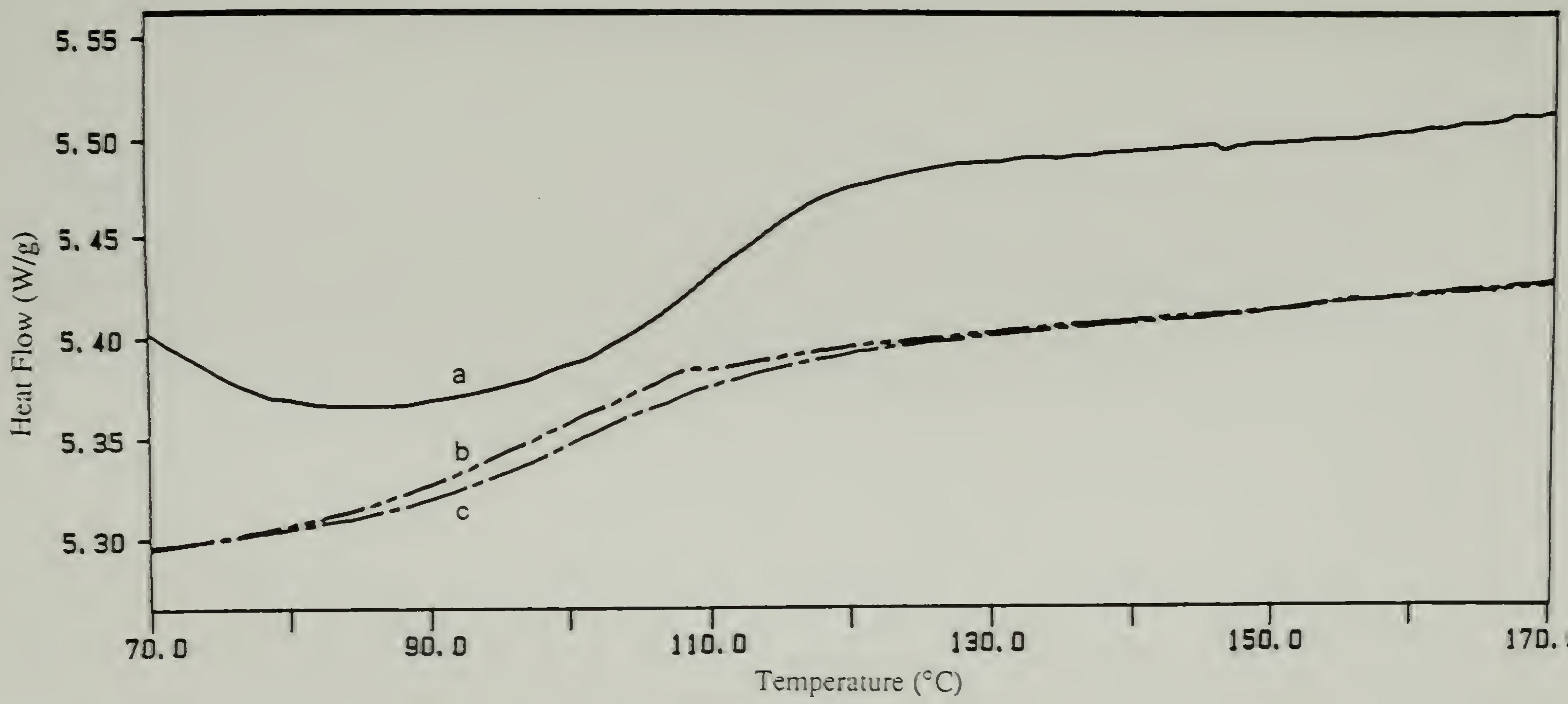

Figure 4.2. Effect of annealing on 50/50 blends of TBPC/PVC-0.

a. previously heated to 200°C and 210°C.
b. annealed at 180°C for 5 minutes.
c. annealed at 180°C for 20 minutes.

T_g and may not be high enough for the high-viscosity polymer system to reach equilibrium. The highest measured T_g after heat treatment was 114°C. This was achieved after heating the sample twice to 210°C at a heating rate of 30°/minute. Beside kinetic barriers, PVC crystallinity needs to be overcome if a one-phase system is to be realized.

Blends of PVC with TCPC show a single, composition-dependent glass transition temperature. T_g's for PVC-0/TCPC-2 blends as a function of TCPC weight fraction are shown in Figure 4.3. TCPC/PVC blends did not show the dependence upon thermal history seen in the TBPC/PVC blends. Several annealing temperatures were used (to as high as 260°C) yet there was no indication of phase separation. Blends of the highest molecular weight materials, PVC-3 and TCPC-2, were also found to be miscible in all proportions.

Along with the experimental data, the predicted T_g's based on Equations (3.1) and (3.2) are shown. Equation (3.2) more closely follows the data, though the experimental T_g's are slightly lower than the theoretical values. Deviations from the predicted values may be explained in terms of excess volume changes upon mixing, the result of interactions or molecular packing. The negative deviation in the TCPC/PVC blends may be caused by inefficient chain packing, leading to increased free volume and a lower glass transition temperature.

The semi-crystalline behavior of PVC may be a factor explaining the T_g deviation from predicted values. The

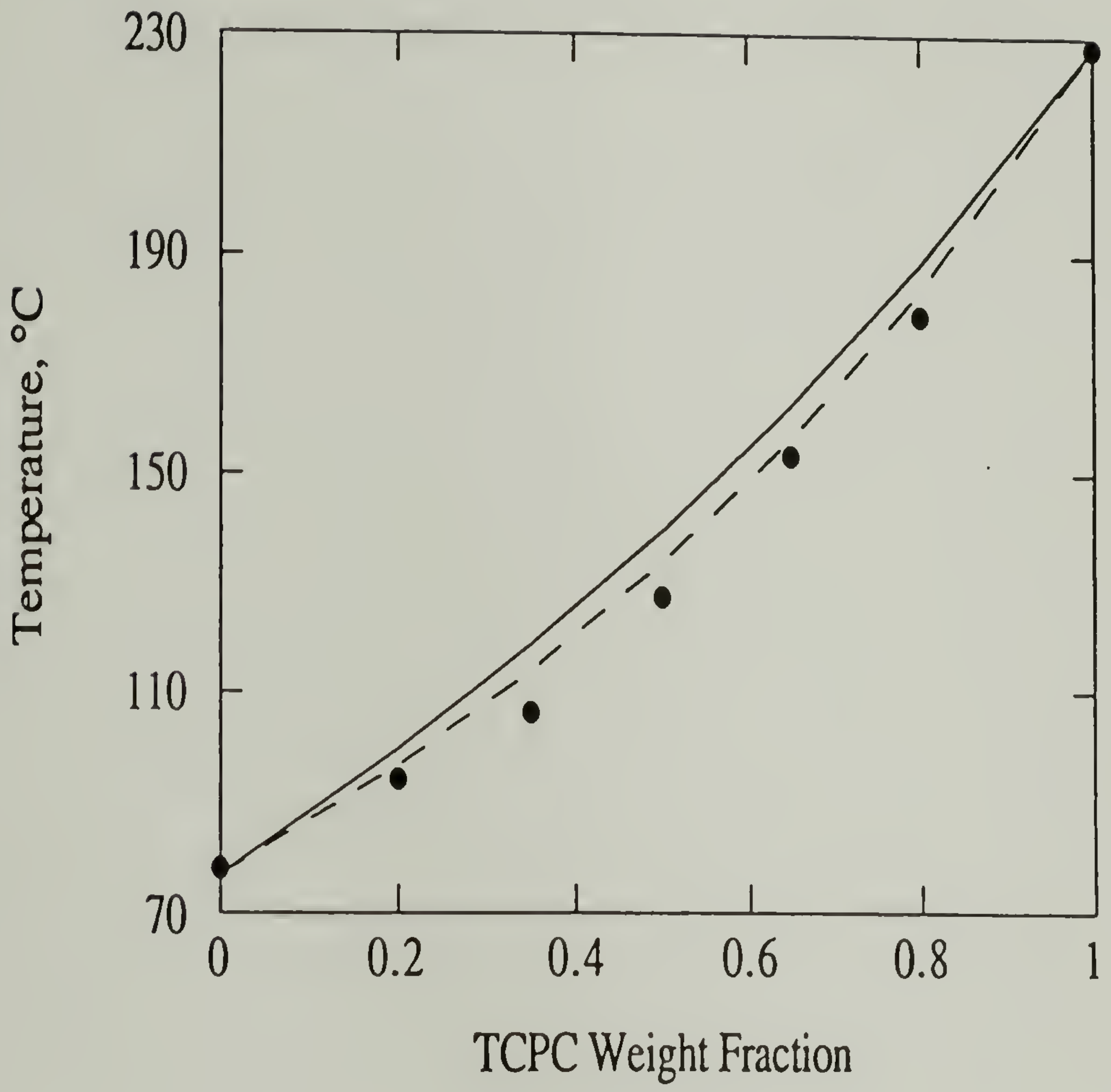

Figure 4.3. Glass transition temperature of TCPC-2/PVC-0 blends. Solid curve, $T_{g,blend}$ predicted by Equation (3-1); dashed curve, blend glass transition temperature calculated from Equation (3-2).

glass transition is an amorphous phase process. Coupling with a crystalline phase can increase the T_g of the amorphous phase. In calculations of blend T_g's, the T_g of semi-crystalline PVC is used. Blends which contain greater than 35% (by weight) TCPC do not exhibit a PVC melt endotherm, and it may be appropriate to use a lower, purely amorphous, PVC T_g in calculations.

The dynamic mechanical spectra of TCPC/PVC blends shows some interesting features (Figure 4.4). In 50/50 (by weight) blends, the DMA loss tangent spectrum has a single T_g at 140°C and two, low temperature relaxations. These two secondary processes have maxima at approximately -35°C and 75°C. These processes correspond to the secondary relaxations of PVC and TCPC, respectively. Since these relaxations are due to localized motions in the polymer backbone, involving 5 to 9 repeat units, they will be sensitive to interactions occurring between the polymers. The presence of two peaks in the low temperature region suggests that the two polymers do not interact strongly.

In the blend containing 75% by weight TCPC, there is an unexpected change in the dynamic mechanical behavior. The PVC *beta*-relaxation peak shifts to -59°C. As the minor component in the blend, PVC may not be able to aggregate or crystallize. This low temperature process may be an amorphous PVC relaxation.

Infrared spectroscopy is a means of identifying specific interactions in polymer blends.[15] The carbonyl

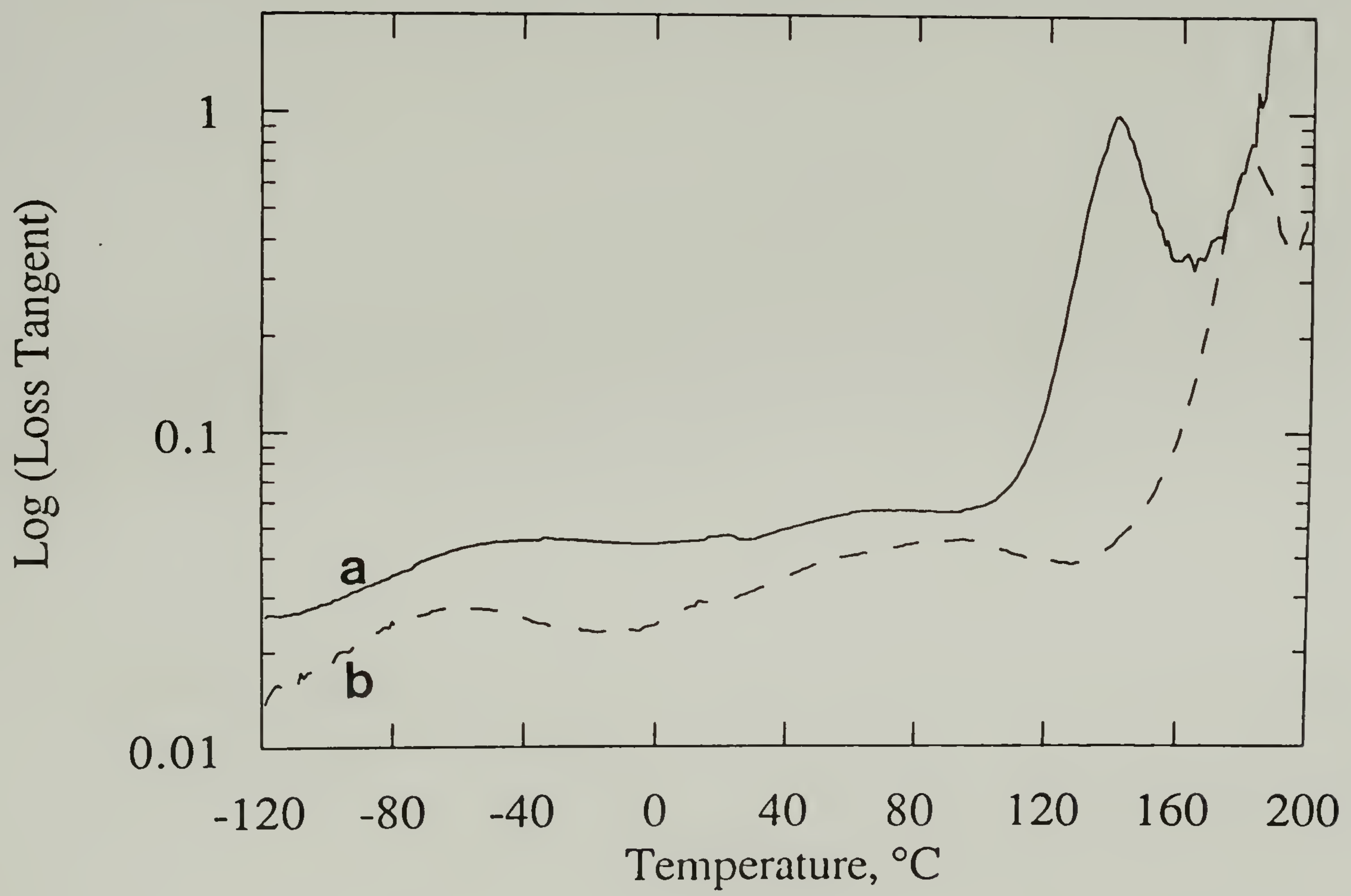

Figure 4.4. Loss tangent of TCPC/PVC blends. (a) 50/50 (by weight) TCPC-2/PVC-0; (b) 75/25 TCPC-2/PVC-0. Measurement frequency is 1 Hz.

stretch band for TCPC/PVC and BPC/PVC blends is shown in Figure 4.5. The high wavenumber shoulder of pure TCPC is due to frozen-in conformations, a result of sample preparation. Comparing the spectra of the two PCs, there is little effect on the carbonyl stretch as a result of blending. The peak values for pure TCPC, 50/50 TCPC/PVC, and 25/75 TCPC/PVC are 1799.8, 1799.3, and 1798.9 cm^{-1}, respectively. The shift is less than 1 cm^{-1}. The same behavior is seen in BPC/PVC blends in which there no phase mixing. If a specific interaction exists between TCPC and PVC, it does not involve the TCPC carbonyl group. The conformational sensitivity of the C-Cl stretch in PVC makes it difficult to interpret the 1-3 cm^{-1} shifts in that characteristic region (600 to 700 cm^{-1}).

Several investigators have studied the decomposition of PVC in its blends with other polymers.[16-18] The degradation behavior of PVC in blends has been found to be effected by its miscibility behavior. The conclusion of these studies is that miscibility may improve the thermal stability of PVC. Figure 4.6 shows the degradation behavior as a function of composition for BPC/PVC and TCPC/PVC blends, respectively. The onset of weight loss in the blends is the same as that for the pure PVC. Above 300°C, weight loss begins. Derivative TGA curves (weight change/temperature change) in both the miscible and immiscible blends show an increase in the temperature at which the maximum rate of weight loss

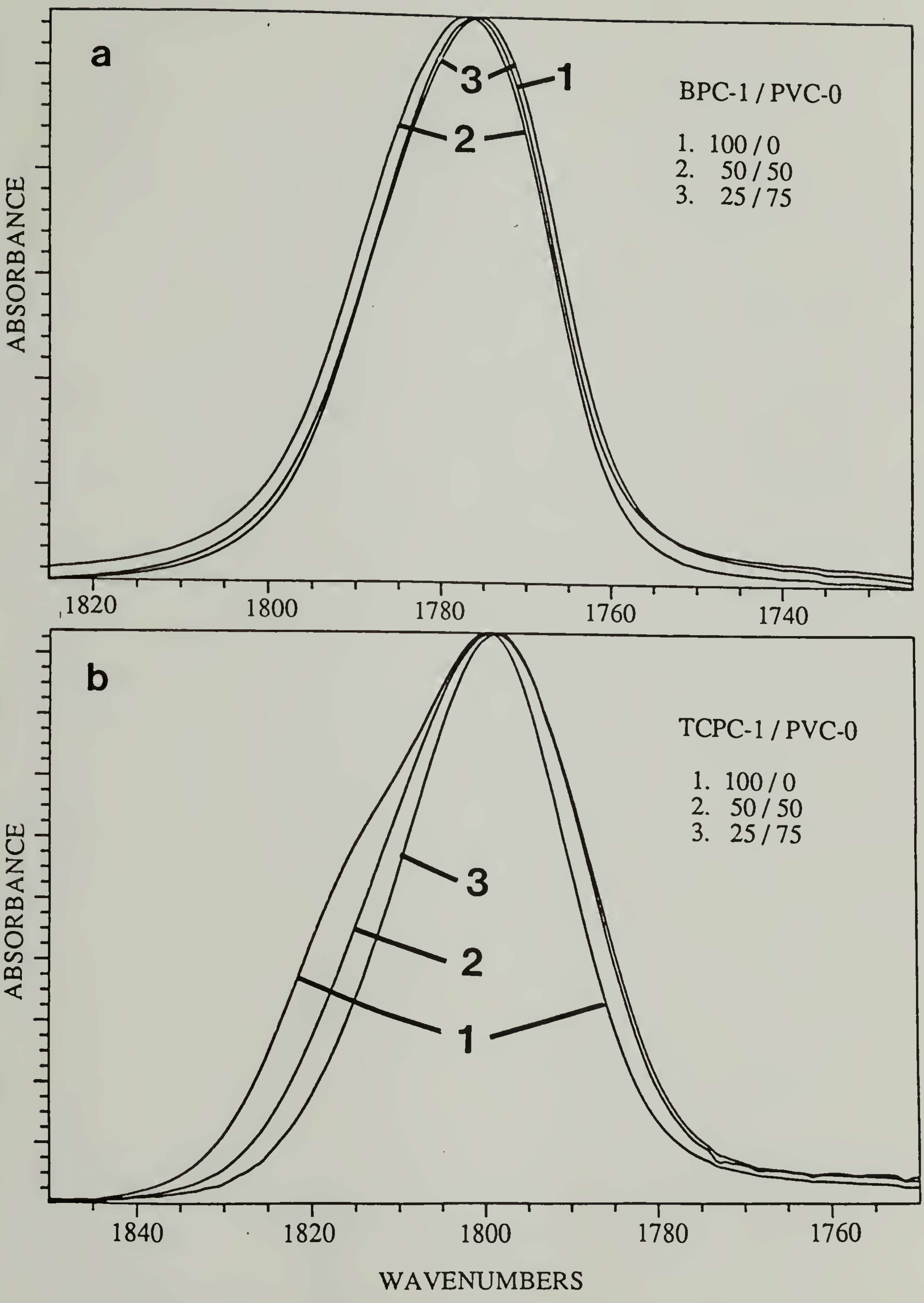

Figure 4.5. Carbonyl stretch region of IR spectrum for (a) BPC/PVC blends and (b) TCPC/PVC blends. Blend ratios are by weight.

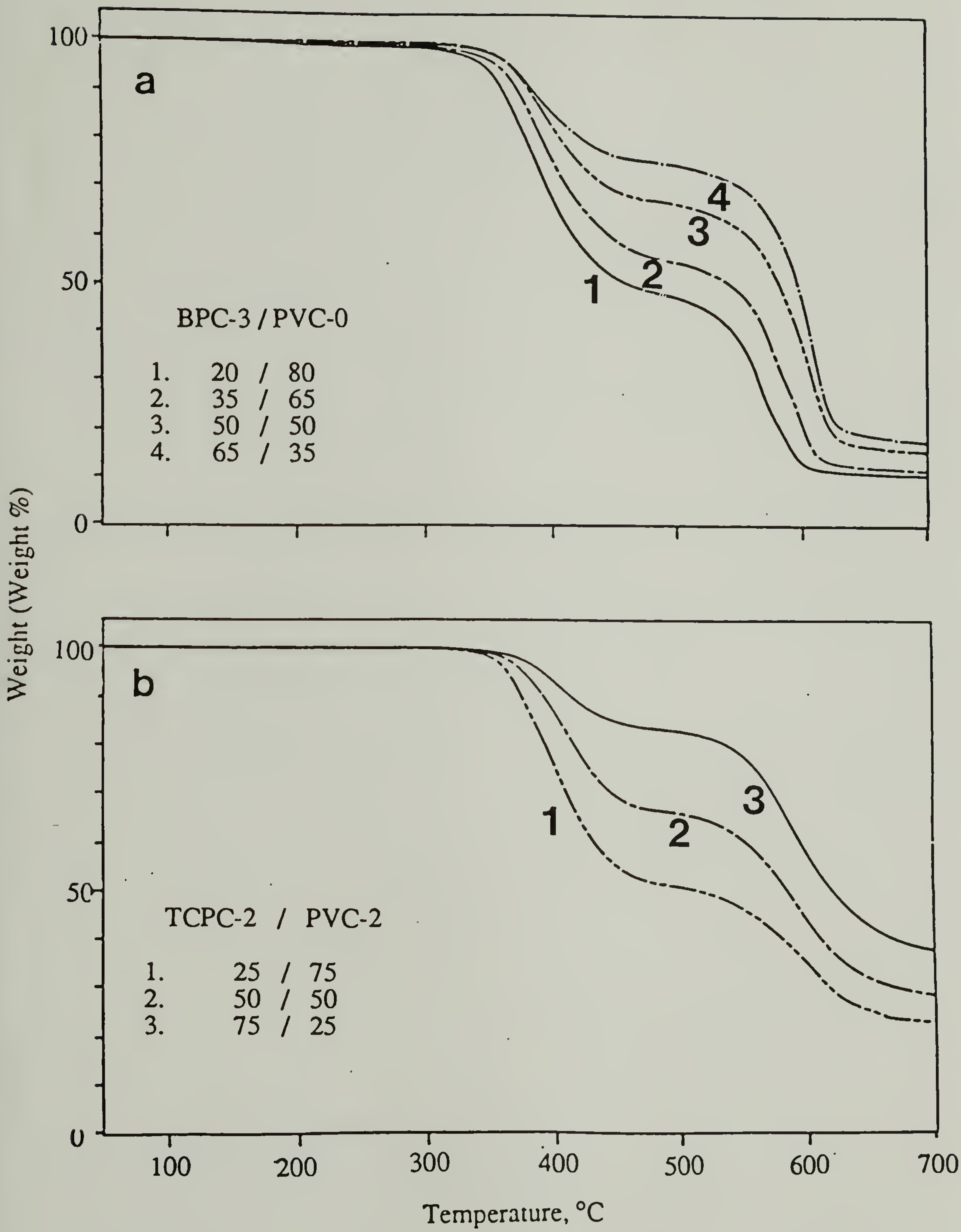

Figure 4.6. Weight loss versus temperature for (a) BPC/PVC blends and (b) TCPC/PVC blends. Heating rate is 20°C/minute. Blends ratios are by weight.

occurs. Addition of TCPC to PVC does not improve the thermal stability of PVC.

The PC/PVC blends provide some limited information about the segmental interaction parameters. Critical values for these parameters ($X_{critical}$) can be estimated from the molecular weight information and use of Equation (1.6). From these calculations, it can be concluded that the $X_{PC,PVC}$'s are greater than or less than the critical values for miscible and immiscible systems, respectively. This is the only statement which can be made about the $X_{PC,PVC}$'s; more information--either from homopolymer-copolymer blends or copolymer-copolymer blends--is needed to determine more precise values of the $X_{PC,PVC}$'s.

Polycarbonates Blended with CPVCs

Blends which contain a polycarbonate homopolymer and a CPVC can be considered $A/B_{1-x}C_x$ copolymer blends. A CPVC, regardless of the chlorination process, can be considered a copolymer of three repeat units: $-CH_2-$, $-CHCl-$, and $-CCl_2-$. A simplification can be made for solution-chlorinated PVCs; solution-CPVCs may be treated as copolymers of vinyl chloride (VC) and 1,2-dichloroethylene (DCE). This assumption is made on the basis of the work of Komoroski *et al.*[19] It was found that chlorine adds almost exclusively to the methylene group of PVC and the content of $-CCl_2-$ groups is negligible until approximately 64% (by weight) chlorine (weight percent chlorine in PVC is 56.8). For a solution-CPVC with a 70% (by weight) loading of chlorine, approximately 7 mole % of the PVC backbone carbons are dichlorinated. This copolymer model for solution-CPVCs has been used in earlier investigations of interaction parameters.[20,21]

Shiomi *et al.*[20] determined the interaction parameter for the VC-DCE pair, $\chi_{VC,DCE}$, to be 0.042. According to the mean field model, the positive value of $\chi_{VC,DCE}$ means that there exists a "repulsive" intramolecular effect within a solution-CPVC. Depending upon the interaction between the polycarbonate repeat unit and each of the vinyl repeat units ($\chi_{PC,VC}$, $\chi_{PC,DCE}$) and x, the fraction of DCE in the solution-CPVC, a miscible blend may result.

In the previous section, the effect of polycarbonate modification on miscibility with PVC was considered. In this section, the chlorination of PVC and its effect on miscibility with PC homopolymers is reported.

Table 4.2 shows the DSC results for 50/50 blends of BPC-3, HFPC, and TMPC-1 with several solution-CPVCs. Annealing temperatures up to 220°C were used. All of the blends show two glass transitions, though slight shifts in T_g's may be present. The glass transition temperature of BPC-3 in the blends is the same as the pure BPC transition temperature. The CPVC-phase, in BPC/CPVC blends containing CPVC-6 through CPVC-8, shows a 3-5°C increase over the neat CPVC T_g. A similar effect is noted in TMPC blends with

Table 4.2. Glass transition temperatures of 50/50 blends of polycarbonates with solution-chlorinated PVCs.

Blend System	Glass Transition Temperature, $^{\circ}C$
BPC-3 / CPVC-4	98 / 150
BPC-3 / CPVC-6	112 / 149
BPC-3 / CPVC-7	122 / 151
BPC-3 / CPVC-8	133 / 152
HFPC / CPVC-4	160 / 94
HFPC / CPVC-6	160 / 106
HFPC / CPVC-8	160 / 128
HFPC / CPVC-10	160 / 178
TMPC-1 / CPVC-3	199 / 95
TMPC-1 / CPVC-4	199 / 99
TMPC-1 / CPVC-6	196 / 108
TMPC-1 / CPVC-8	197 / 131
TMPC-1 / CPVC-9	200 / 154
TMPC-1 / CPVC-10	198 / 179

CPVC-4 and CPVC-5. There is no shift present in either the CPVC-phase T_g or PC-phase T_g in HFPC/CPVC blends. In the BPC and TMPC blends, there may be low molecular weight polycarbonate fractions dissolved in the CPVC-phase.

Lowering the molecular weight of the PC does not change the results. BPC-0 and TMPC-0 blends with solution-CPVCs are also phase separated. Like the higher molecular weight blends, the CPVC-phase has a T_g which is 4^oC greater than the pure CPVC, while the T_g of the PC phase is unaffected.

These results for BPC and TMPC blends with CPVC contrast with those of Braun *et al.*[2] in two respects. First, Braun found that certain compositions (10/90 and 90/10 PC/CPVC) of these PCs blended with a CPVC having 60 weight % chlorine were miscible. This might be explained by the use of a lower molecular weight CPVC used in that study. Second, Braun discussed miscibility as a function of vinyl-polymer chlorine content and blend composition, and above 60 weight % chlorine, all blends were miscible. The conclusion that increased chlorination of a vinyl polymer enhances miscibility with BPC and TMPC did not take into consideration the vinyl polymers chosen for the study. The highly chlorinated materials used by Braun were vinyl chloride-vinylidene chloride copolymers. The behavior of BPC or TMPC blended with solution-CPVCs is the opposite of polycarbonate/vinyl chloride-vinylidene chloride blends. The source of miscibility in blends of vinyl chloride-vinylidene chloride copolymers with BPC and TMPC may be a strong copolymer effect. It is known that PVC and poly(vinylidene chloride) are immiscible.[22]

TBPC blends with solution-CPVCs show a single glass transition in the measurable temperature range (< 230°C). The T_g increases as the quantity of TBPC in the blend increases. The composition dependence of T_g for some TBPC/ solution-CPVC blends is shown in Figure 4.7. In general, 25% (by weight) loading of TBPC leads to an increase in the CPVC T_g of 11° to 15°C; 50% loading increases the T_g by 40°C over the pure CPVC transition temperature. The CPVC-9 data is well fitted by Equation (3.1). As chlorine content in the CPVC decreases, the blend glass transition temperatures show an increasing negative deviation from predicted values.

TBPC blends with PVC and CPVC cannot be adequately studied because of the thermal instability of the vinyl chloride polymers. The results for these blends may not reflect equilibrium behavior.

TCPC is miscible with CPVCs having chlorine contents up to 70.2 weight % (CPVC-11). This is indicated by a single T_g in DSC experiments as well as by the optical clarity of the film samples. Blends of TCPC/CPVC-12 cast from THF and methylene chloride were cloudy, and this system was deemed immiscible. The glass transition temperatures of 50/50 (by weight) blends of TCPC with several solution-CPVCs are shown in Figure 4.8.

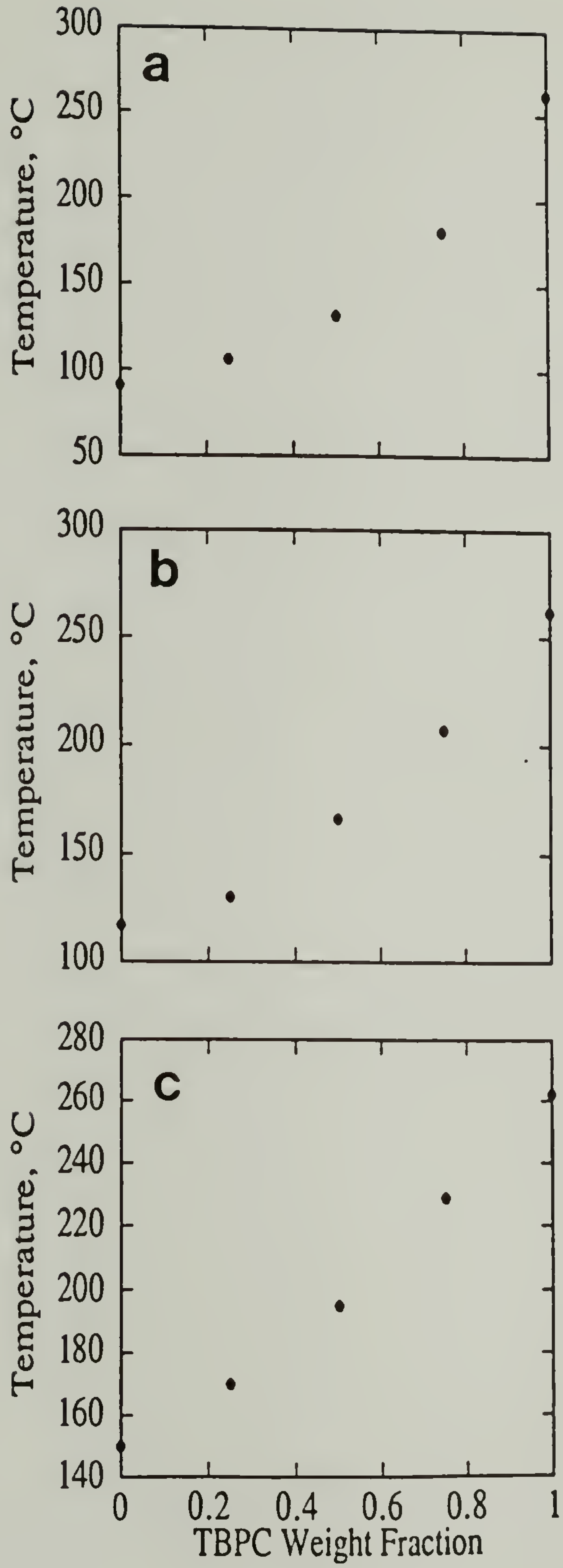

Figure 4.7. Glass transition temperatures for blends of TBPC with CPVC-3 (a), CPVC-7 (b), and CPVC-9 (c).

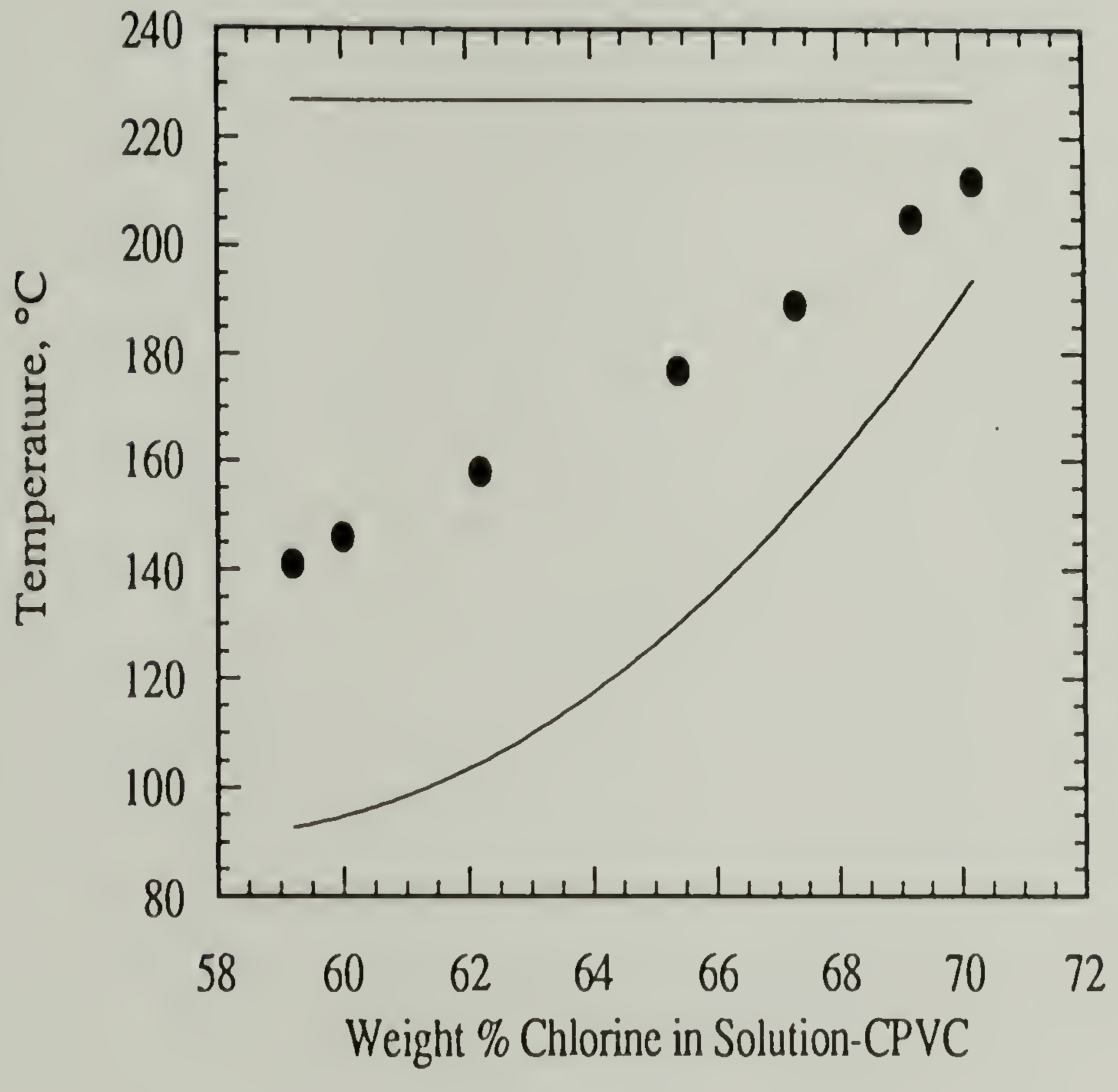

Figure 4.8. Glass transition temperature of 50/50 (wt/wt) TCPC/solution-CPVC blends.

Like the TCPC/PVC blends, infrared analysis of the carbonyl stretch region does not implicate this functional group as a contributor to blend miscibility. If a specific interaction exists, it is between the TCPC phenyl rings and the methyne protons or chlorines of solution-CPVC.

Differences in CPVC microstructure did not effect miscibility behavior with the PC homopolymers. In Figure 4.9, the behavior of TCPC/DSP-68 and BPC/DSP-63 are shown. In spite of their low molecular weight, the slurry-chlorinated CPVCs were immiscible with BPC, HFPC, and TMPC. Blends with TCPC had a single, composition dependent glass transition temperature. In the miscible blends with DSP-68 (Figure 4.9a), the glass transition breadth was large, between 14^{o} and 18^{o}C. This is still lower than the transition breadth of pure DSP-68, which is greater than 30^{o}C. Thus, the heterogeneity of the CPVC is still exhibited in miscible blends.

Discussion

In PC/PVC blends, the effect of substitution on the bisphenol-A repeat unit was studied. Methyl substitution at the 3,3',5,5' phenyl positions did not affect miscible behavior. Changing the polarity of the isopropylidene group by substituting $-CF_3$ for the $-CH_3$ did not lead to miscible blends with PVC and the CPVCs. Paul[23] has advanced the argument that the changes in electron density with halogen

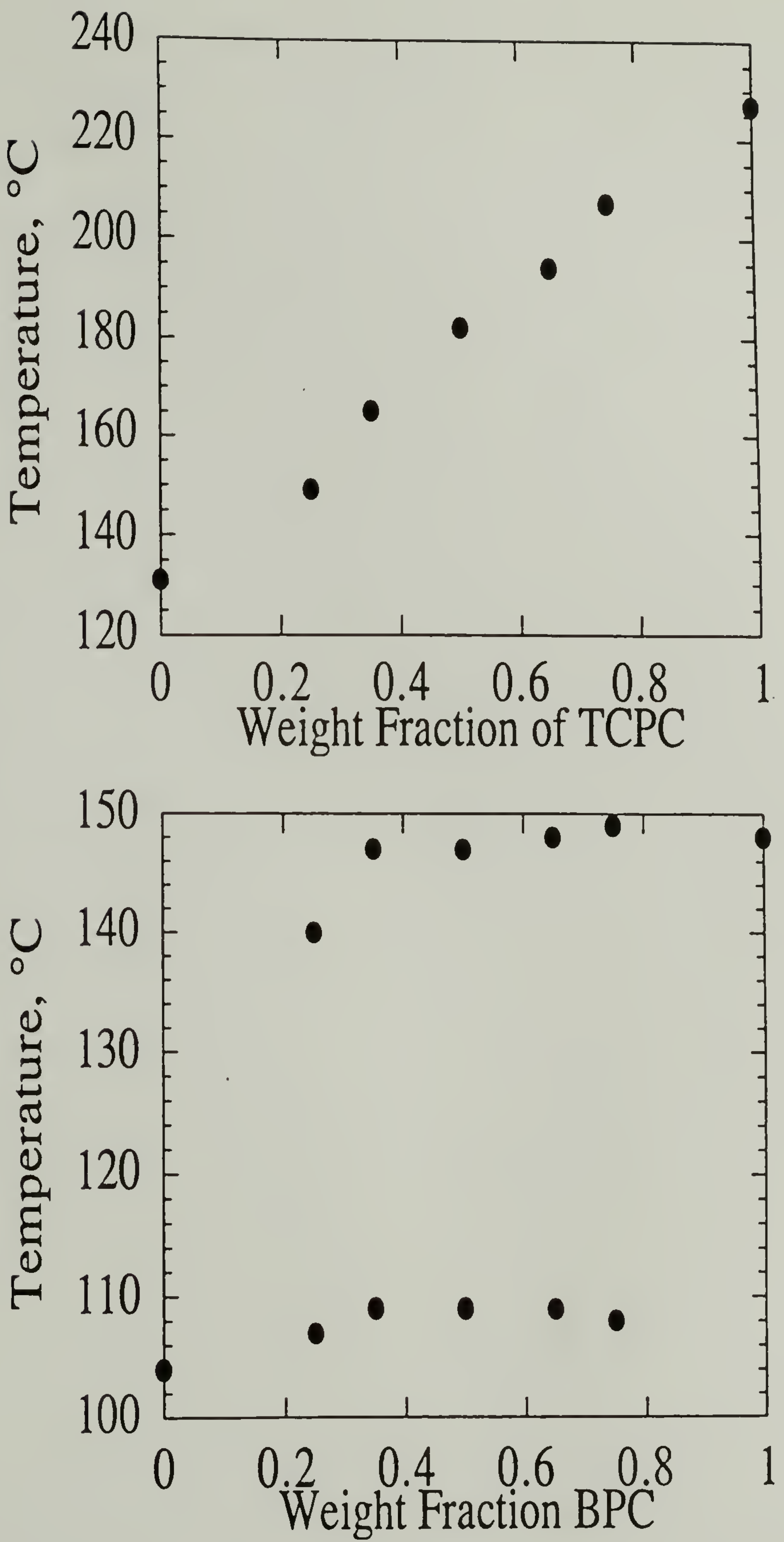

Figure 4.9. Polycarbonate blends with slurry-CPVCs. (a) TCPC-2/DSP-68; (b) BPC-2/DSP-63.

substitution in the PC leads to favorable interactions with polystyrene, PMMA, and polyesters. While halogen (-Cl, -Br) substitution on the phenyl rings leads to miscible blends with CPVCs, halogen substitution at the isopropylidene group was not as effective. While fluorine substitution results in a more highly polar PC repeat unit, the inductive effect is not great enough to influence the electron density distribution throughout the phenyl ring system. Another factor which may contribute to the lack of interaction between HFPC and PVC is the shielding of the quaternary carbon. Its positive polarity may make it susceptible to interaction with PVC, but the phenyl rings and the fluorinated methyl groups hinder the interaction.

Schnell[24] recognized early that the carbonate group cannot be an important factor affecting miscibility, due to its small size relative to the rest of the PC repeat unit. Thus, the miscibility found in the TCPC and TBPC blends must be due to PVC interactions with the phenyl rings. The halogen-substituted rings may be electron deficient leading to a favorable interaction with the chlorine of PVC.

The conclusion reached by Braun and Woo--that halogenation of a polymer enhances its miscibility with PCs --is not general. The distribution of the halogen within the polymer is a significant factor. In the case of poly(vinyl chloride-*co*-vinylidene chloride) (VC-VDC), intramolecular effects are important, that is, VC and VDC repeat units interact unfavorably. In randomly chlorinated PVCs, with chlorine loadings of up to 65% by weight, the materials closely resemble VC-DCE copolymers. These data suggest that $\chi_{VC,VDC} > \chi_{VC,DCE}$ since VC-VDC copolymers are miscible with both BPC and TMPC.

An interesting feature of these results is the immiscible behavior of TCPC with highly chlorinated PVC. While PVC is miscible with TCPC, increased chlorination of CPVC ultimately leads to phase separation.

In the solution-CPVCs, there are two forces at work which affect miscibility with TCPC. There is the attractive interaction between vinyl chloride and TCPC repeat units, and the intramolecular, repulsive interaction between vinyl chloride and 1,2-dichloroethylene repeat units. Each will contribute to χ_{blend}, and the relative contribution of each will change with x, the fraction of DCE repeat units. For example, at small x, $\chi_{TCPC,VC}$ might be expected to be the predominant factor, while at high x, close to the miscible-immiscible boundary, $\chi_{VC,DCE}$ will dominate. The effect of these two contributions is shown schematically in Figure 4.10.

As x increases in Equation (3.3), the favorable contribution to χ_{blend} from $\chi_{TCPC,VC}$ decreases and the unfavorable contribution due to $\chi_{TCPC,DCE}$ increases. The contribution due to VC-DCE intramolecular repulsion, which is always favorable to mixing, reaches its maximum at x =

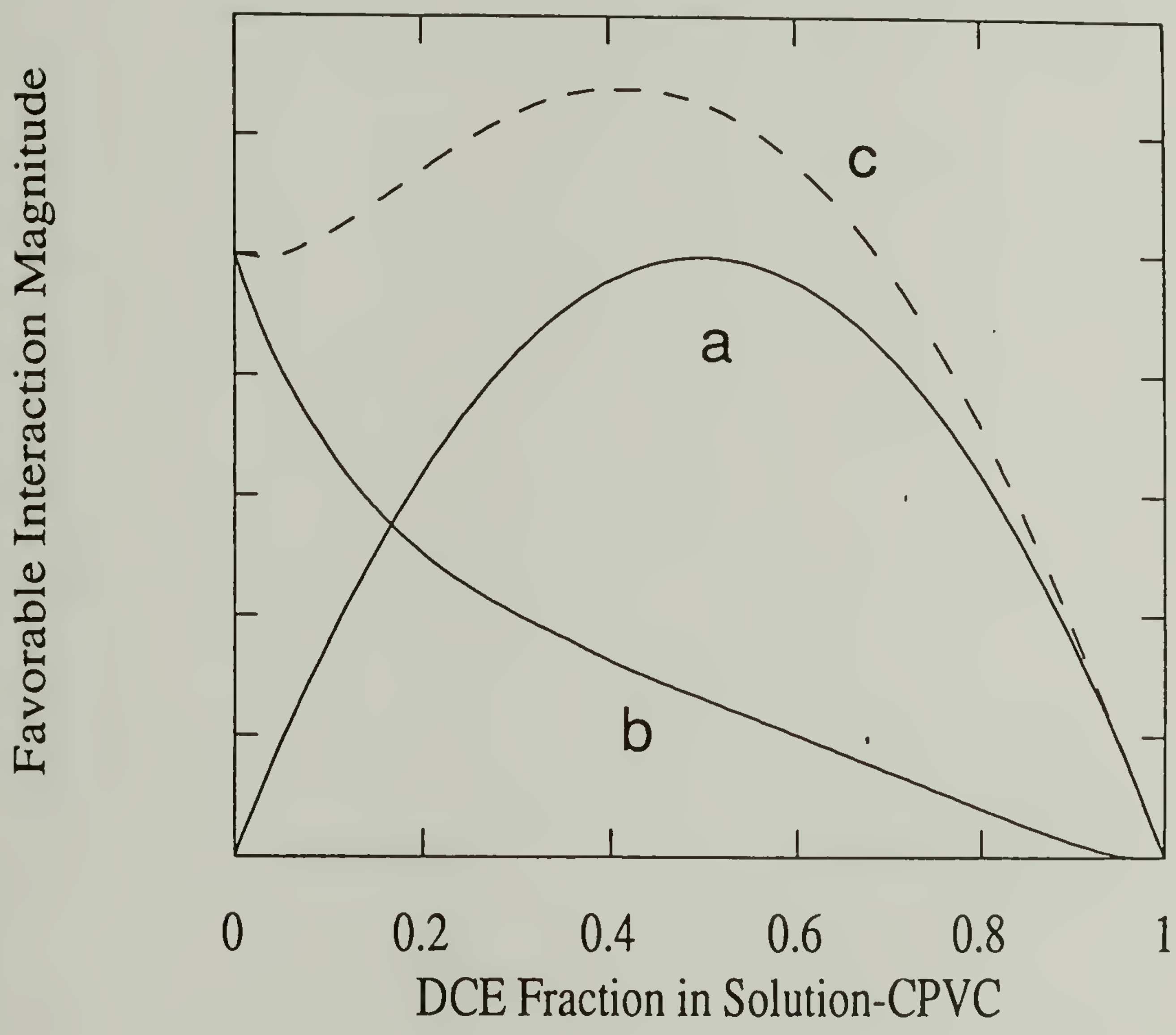

Figure 4.10. Contribution from (a) intramolecular and (b) intermolecular effects to the favorable interaction (c) between TCPC and solution-CPVCs.

0.5. As x is increased above 0.5, the contributions from $\chi_{VC,DCE}$ and $\chi_{TCPC,VC}$ to χ_{blend} diminish and $\chi_{TCPC,DCE}$ becomes dominant.

This is evidence that a copolymer effect is producing miscibility in TCPC blends with solution-chlorinated PVCs. Such behavior is probably present in the TBPC/solution-CPVC blends as well. In blends with the other polycarbonates--BPC, HFPC, and TMPC--the intramolecular repulsion of VC-DCE interactions is not sufficient to overcome the contributions of $\chi_{PC,VC}$ and $\chi_{PC,DCE}$.

These homopolymer/copolymer blends do not provide enough information to estimate χ_{ij}'s using the mean field approach. Copolymerization of the polycarbonates, and study of these PCs with solution-CPVCs, the segmental interaction parameters $\chi_{PC,VC}$ and $\chi_{PC,DCE}$ can be determined. This is the topic of the following two chapters.

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CHAPTER 5

BLENDS OF POLYCARBONATE COPOLYMERS WITH PVC AND CPVC

It has been shown that $\chi_{\mathrm{BPC,TCPC}}$ and $\chi_{\mathrm{TMPC,TCPC}}$ are positive, and the homopolymer polycarbonates formed two-phase blends. It has also been noted that the interaction parameter for vinyl chloride (VC) contacts with 1,2-dichloroethylene (DCE)--the comonomer model used for solution-chlorinated PVCs--is positive ($\chi_{\mathrm{VC,DCE}} = 0.042$).[1] Therefore, the potential exists for (polycarbonate copolymer/solution-CPVC) blends to form miscible blends, the mixing being driven by intramolecular repulsions within each copolymer.[2-4]

The copolymer χ_{ij}'s which have been determined so far cannot be used to predict the phase behavior of (PC copolymer/ solution-CPVC) blend systems. An $A_{1-x}B_x/C_{1-y}D_y$ system (x and y refer to the fractional composition of monomer residues B and D, respectively, within each of the copolymers) requires six segmental interaction parameters for calculation of χ_{blend}. There are four χ_{ij}'s, each PC repeat unit with both VC and DCE ($\chi_{PC-1,VC}$, $\chi_{PC-2,VC}$, $\chi_{PC-1,DCE}$, $\chi_{PC-2,DCE}$), which need to be determined. The mean field approach allows for the estimation of five of the six interaction parameters of an $A_{1-x}B_x/C_{1-y}D_y$ system if one of the six χ_{ij} is known (Equation 1.9). This method will be employed in the next chapter to calculate χ_{ij}'s from copolymer/copolymer miscibility maps.

In this chapter, the focus will be on the phase behavior of polycarbonate copolymers blended with PVC and CPVCs. In TCPC-containing, polycarbonate copolymers, it is expected that miscibility with PVC will be enhanced as TCPC content is increased due to the miscibility of these repeat units.

Characterization of the copolycarbonates was discussed in Chapter 2. There are two series of TCPC-containing copolymers (BPC-TCPC and TMPC-TCPC), a 50/50 HFPC-TMPC copolymer (HFPC-TMPC-50), and a 50/50 BPC-TBPC copolymer (BPC-TBPC-50). The presence of miscibility windows in blends of these copolymers with solution-CPVCs will provide information necessary to estimate the segmental interaction parameters.

Experimental

Three BPC-TCPC copolymers containing 25, 50, and 75 mole percent TCPC and three TMPC-TCPC copolymers having 41, 58, and 91 mole percent TCPC were blended in 50/50 weight ratio with PVC and CPVCs. Samples were prepared by (1) dissolution in THF (4% w/v) and casting in glass dishes, (2) dissolution in methylene chloride (4% w/v) and casting in glass and aluminum dishes, and (3) dissolution in THF (4% w/v) and precipitation in an eleven-fold excess of methanol. Drying was carried out in a vacuum oven at 50°C. Films cast from THF solution were cycled to 120°C to remove residual THF. This thermal treatment resulted in slight discoloration of the films, indicative of some degradation. This degradation, however, was minimal; the films were still soluble in THF and the T_g behavior was not effected, as compared with precipitated blends and those cast from methylene chloride.

All BPC-TCPC and TMPC-TCPC copolymers were blended in 50/50 weight proportions with PVC-1 and all the solution-CPVCs. Several copolycarbonate/solution-CPVC pairs were blended in varying compositions to study the composition dependence of miscibility.

BPC-TCPC Copolymers Blended with PVC and Solution-CPVCs

Glass transition temperatures measured by differential scanning calorimetry (DSC) for 50/50 (by weight) blends of BPC-TCPC-copolymers with PVC and solution-CPVCs are shown in Figure 5.1. Between BPC-TCPC-50 and BPC-TCPC-75, these copolymers begin to exhibit single-phase behavior with PVC. In terms of X_{blend}, as the fractional content of TCPC repeat units in BPC-TCPC copolymer increases, x, X_{blend} becomes less than X_{critical} in the range $0.50 < x < 0.75$.

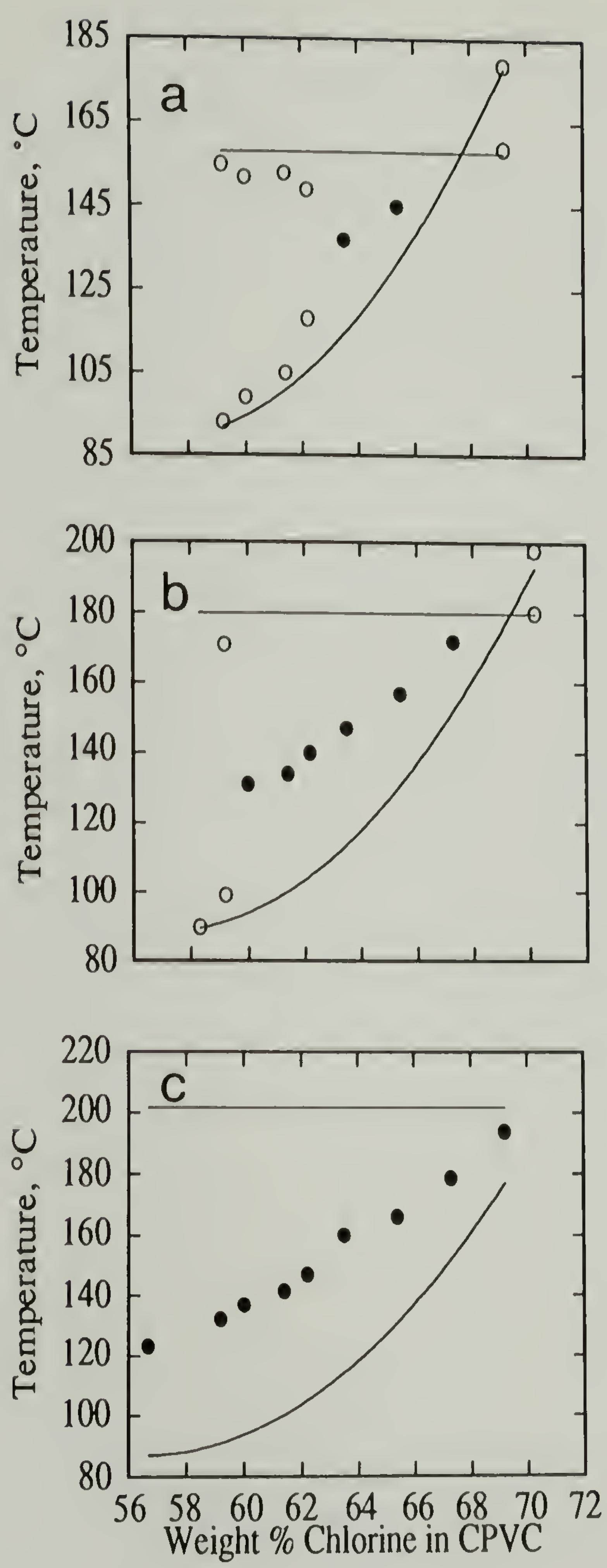

Figure 5.1. Glass transition temperature of 50/50 (wt/wt) blends of BPC-TCPC copolymers with solution-CPVCs. a, BPC-TCPC-25; b, BPC-TCPC-50; c, BPC-TCPC-75.

$X_{critical}$ for these blends is 0.005. To calculate $X_{critical}$, an assumption is made regarding the degrees of polymerization of the copolycarbonates. There is a disparity of size between the PVC and PC repeat units. Using the formulae of Bondi[5] and Van Krevelen[6] for the calculation of molar volumes, the volume ratio of PC to PVC is approximately 5 to 1. Thus, the degree of polymerization of PCs determined from the molecular weight information is increased five-fold in calculations of $X_{critical}$.

In 50/50 blends of BPC-TCPC-25 with solution-CPVCs, there exists a miscibility window between 0.24 and 0.66 mole fraction DCE content (Figure 5.1a). The two CPVCs which show miscible behavior, CPVC-7 and CPVC-8, have T_g's 30° and 43°C below the polycarbonate T_g. It is not likely that the single T_g is due to two mixed phases having nearly similar T_g's. The precise location of the upper limit of the miscibility window, with respect to DCE content in the CPVC, cannot be determined; the polycarbonate copolymer and CPVC-9 have similar T_g's (within 10°C) making assessment of miscibility by the single-T_g criterion difficult. The films of CPVC-9/BPC-TCPC-25 were transparent, but this is not a sufficient indicator of blend miscibility.

As TCPC content increases in the BPC-TCPC copolymer, so does the width of the miscibility window. In Figure 5.1b, the copolycarbonate BPC-TCPC-50 is blended with the solution-CPVCs. The miscibility window is expanded, now extending from 13 mole % to nearly 70 mole % DCE repeat units in the CPVC. BPC-TCPC-75 is miscible with PVC (Figure 5.1c) and all solution-CPVCs up to CPVC-10.

The data gaps at high chlorine contents are due to the similarity of T_g's of the copolycarbonates and solution-CPVCs. Coincidentally, those blends for which the difference ($T_{g,PC}$ - $T_{g,CPVC}$) approaches zero lie close to the miscibility window boundary at high DCE contents. The difference between polycarbonate and solution-CPVC T_g's can be plotted versus copolymer composition. This is shown in Figure 5.2. A trough representing $T_{g,PC} = T_{g,CPVC}$ starts at approximately $x = 0.44$ (x = DCE mole fraction in the CPVC) in blends with BPC (y = TCPC fraction in copolycarbonate = 0) and extends to 0.82 (mole fraction) DCE for TCPC ($y = 1$). The Figure shows that as copolymer composition moves away from the minima, the difference in T_g quickly rises. This is due to the rapid change in solution-CPVC T_g with changing chlorine content, particularly at high chlorine levels.

Annealing temperatures up to 230°C were used to treat the samples. Anneal times at this high temperature were short, 0-10 minutes. At lower temperatures, for example, 160°C, anneal times up to and exceeding 60 minutes could be used. Typically, 20-30 minutes was used at these lower temperatures. Another type of pretreatment was heating the sample to a higher temperature than used for annealing, such as 240°C, followed by rapid cooling. This treatment was used to see if phase separation could be induced at these elevated temperatures.

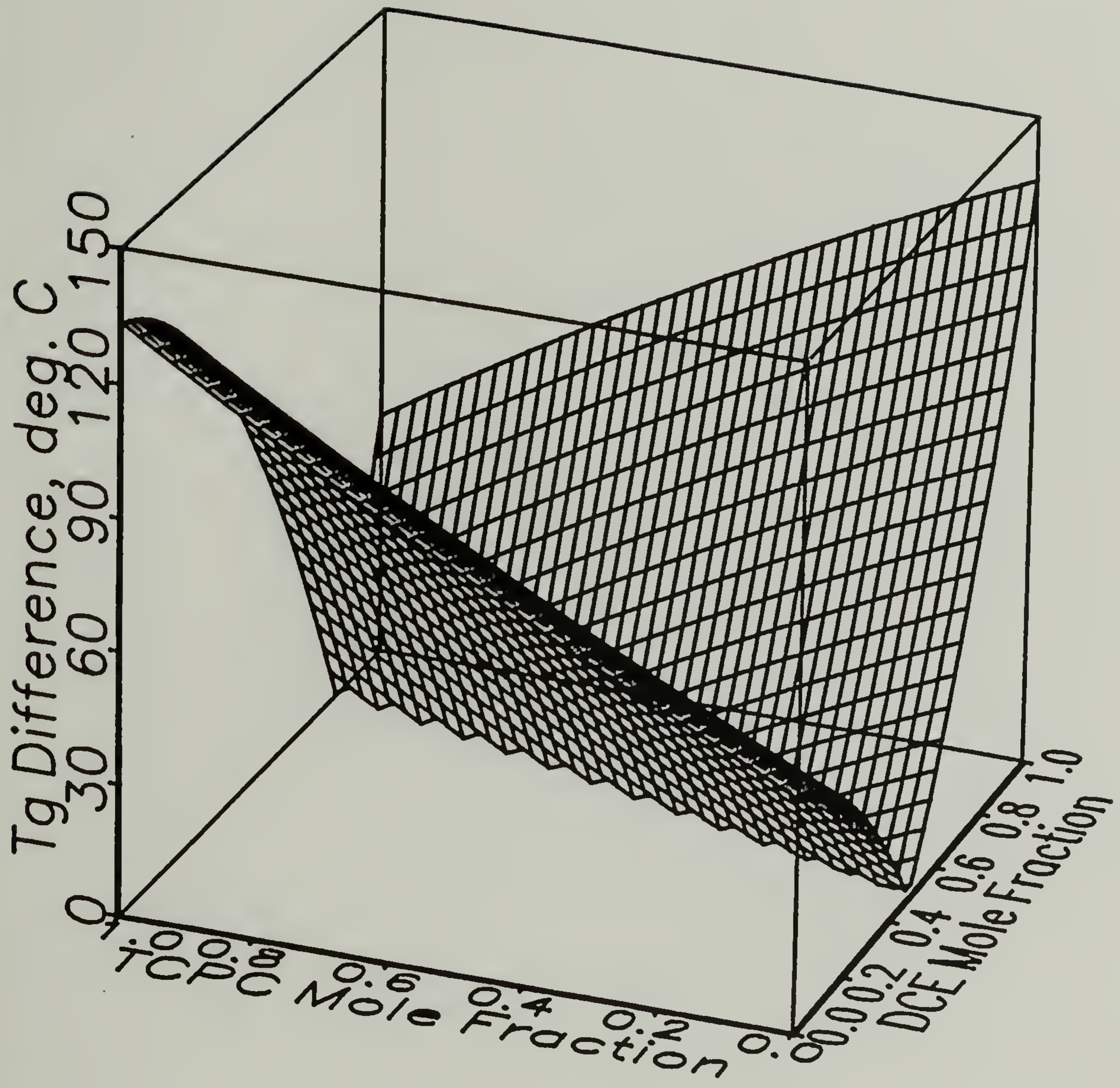

Figure 5.2. Glass transition temperature difference between BPC-TCPC-copolymers and solution-CPVCs.

Because of the wide glass transition temperature range of these polymers, not all samples could be annealed over the same temperature range. Vinyl copolymers with low levels of added chlorine blended with BPC and low TCPC-content polycarbonate copolymers were annealed over the widest temperature range. Blends of high-chlorine content copolymers could only be studied in a narrow temperature range. This is illustrated in Figure 5.3. If it is assumed that these polymers form miscible blends, a "blend glass transition temperature surface" can be drawn as a function of copolymer composition with blend composition held constant. In Figure 5.3, the Equation (3.1) was used to determine the T_g's of 50/50 (by weight) blends of BPC-TCPC copolymers with solution-CPVCs (VC-DCE copolymers). If a degradation ceiling of 250°C is added to this Figure, it is seen that the blends of polymers high in TCPC- and DCE-content have a limited temperature range available for annealing studies. Also, at these high temperatures, the period of time for annealing will need to be reduced so that decomposition does not occur during annealing.

The miscibility boundaries in blends which contain BPC-TCPC-25 and BPC-TCPC-50 were found not to change with increasing annealing temperature. Because of the limitations discussed above regarding annealing temperatures and blend T_g's, it is the low-DCE boundary of the miscibility window which could be thoroughly tested. Annealing at temperatures from 160°C to 220°C did not reveal

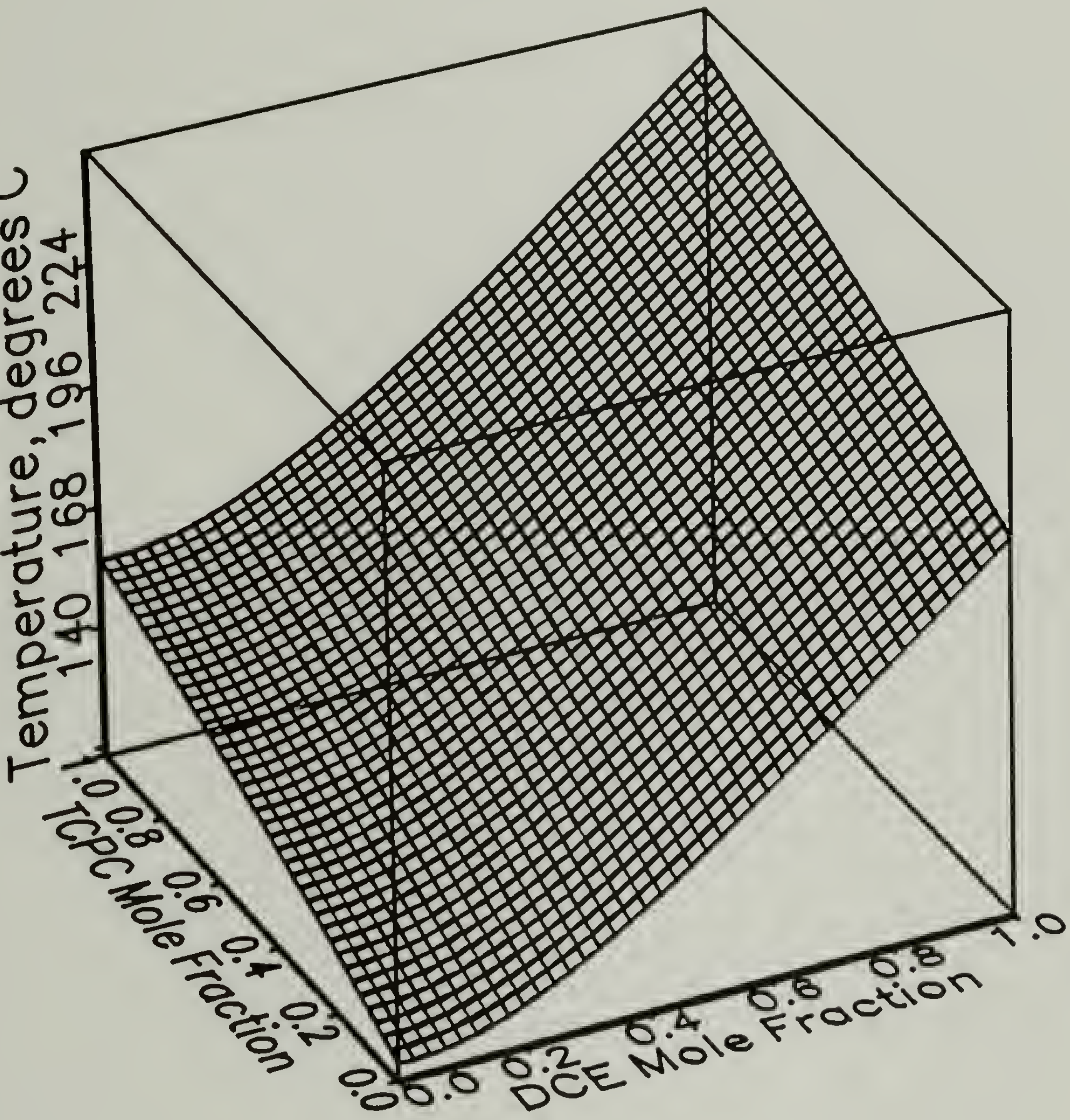

Figure 5.3. Theoretical glass transition temperatures for 50/50 (wt/wt) blends of BPC-TCPC-copolymers / solution CPVCs. Equation (3.1) is used to calculate $T_{g,blend}$.

phase separation. Other studies have shown a decrease in the size of the miscibility window with increasing temperature.[7] This is expected in those systems exhibiting LCST behavior. In these blends, an LCST could not be found within the temperature range studied.

The miscibility window is created by the action of several factors. There is the favorable interaction between vinyl chloride and TCPC repeat units. This attractive force will decrease as the content of VC and TCPC repeat units decreases within their respective copolymers. This cannot be the primary source of interaction leading to a miscibility window. If it were, BPC-TCPC-25 should be miscible with PVC. Thus, the dominant factor leading to miscibility is the intramolecular repulsive effects within the copolymers. This is due to the positive values of $\chi_{BPC,TCPC}$ and $\chi_{VC,DCE}$. That the window occurs in BPC-TCPC-25 blends in a VC-DCE composition range where the intramolecular effect is at a maximum adds weight to the conclusion that a "copolymer effect" is driving miscibility in these copolymer/copolymer blends.

In blends exhibiting a miscibility window, segmental interaction parameters can be calculated if the polycarbonate copolymer is assumed to be a homopolymer. This assumption leads to an A/BC system. With two miscibility window boundaries and $\chi_{VC,DCE}$ known, $\chi_{PC,VC}$ and $\chi_{PC,DCE}$ can be calculated using Equation (3.3). To calculate $\chi_{critical}$, the following degrees of polymerization were used: $N_{BPC\text{-}TCPC\text{-}25} = 160$, $N_{BPC\text{-}TCPC\text{-}50} = 196$, $N_{CPVC} = 1800$. $\chi_{critical} = 0.0053$ for BPC-TCPC-25 blends and $\chi_{critical} = 0.0045$ for BPC-TCPC-50 blends. The miscibility window boundaries chosen for calculations are $x_1 = 0.3$, $x_2 = 0.6$ for BPC-TCPC-25 blends, and $x_1 = 0.12$, $x_2 = 0.65$ for BPC-TCPC-50 blends. The estimated PC-VC and PC-DCE interaction parameters are

$$\chi_{BPC\text{-}TCPC\text{-}25,VC} = 0.013 \qquad \chi_{BPC\text{-}TCPC\text{-}25,DCE} = 0.017$$
$$\chi_{BPC\text{-}TCPC\text{-}50,VC} = 0.008 \qquad \chi_{BPC\text{-}TCPC\text{-}50,DCE} = 0.018.$$

The effect of varying each of the χ_{ij}'s is shown in Figures 5.4 to 5.6. The effect of changing $\chi_{VC,DCE}$ is shown in Figure 5.4. For the BPC-TCPC-25 system, a very small decrease, less than 0.005 ($\chi_{VC,DCE} = 0.037$), in this interaction parameter will cause the miscibility window to close. The BPC-TCPC-50 system can tolerate a greater decrease in $\chi_{VC,DCE}$, but if it is below 0.028, the window disappears. In both systems, the window of miscibility becomes narrower and converges rapidly as $\chi_{VC,DCE}$ decreases incrementally. When $\chi_{VC,DCE}$ values are greater than 0.080, there is little change in the width of the miscibility window due to the repulsive effects of $\chi_{PC,VC}$ and $\chi_{PC,DCE}$.

Increasing $\chi_{PC,VC}$ and $\chi_{PC,DCE}$ will also lead to the loss of the miscibility window (Figures 5.5 and 5.6). When these interaction parameters reach values less than or equal to 0.005, the window extends to the pure vinyl polymer

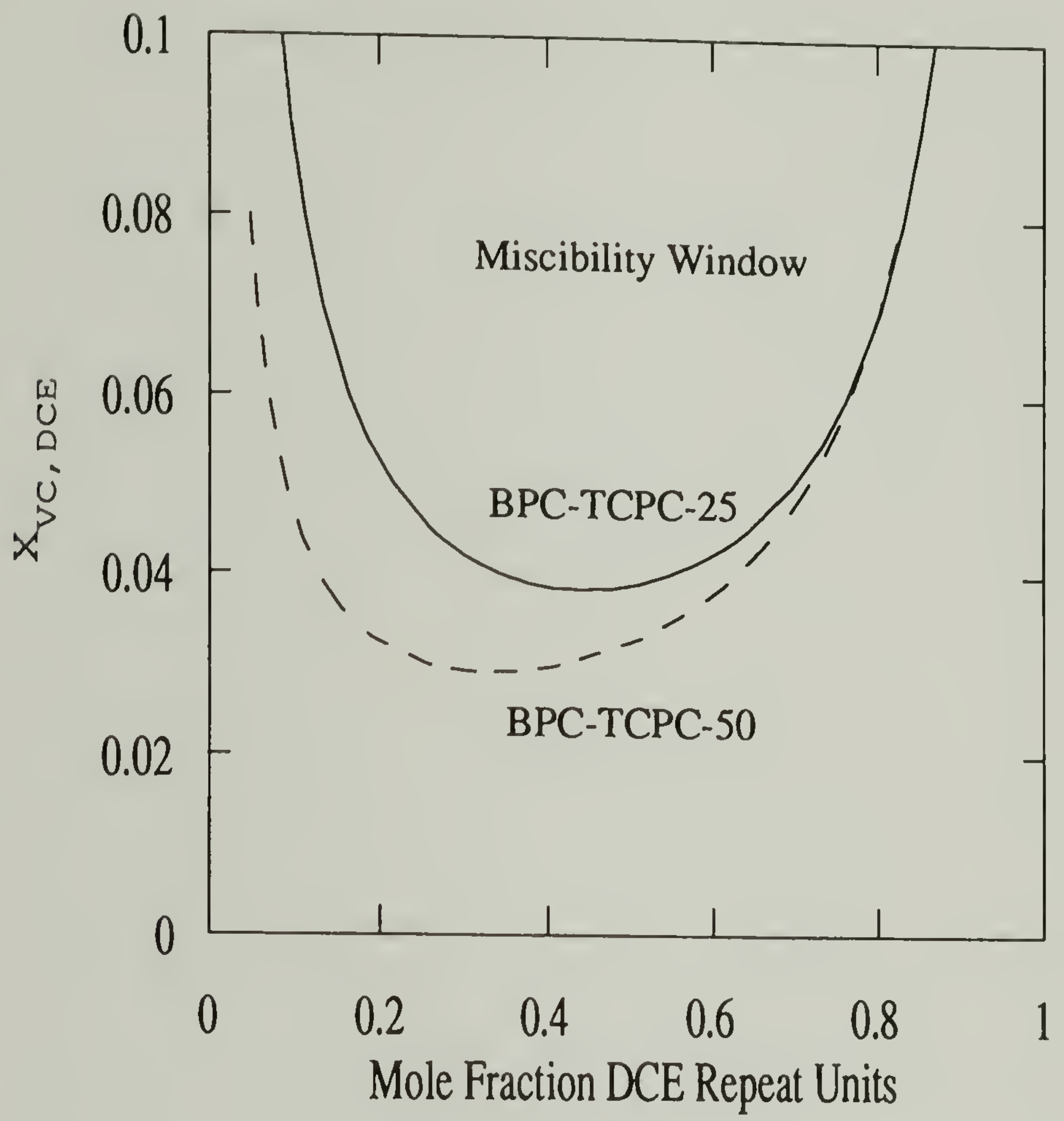

Figure 5.4. Effect of varying $X_{VC,DCE}$ on miscibility window.

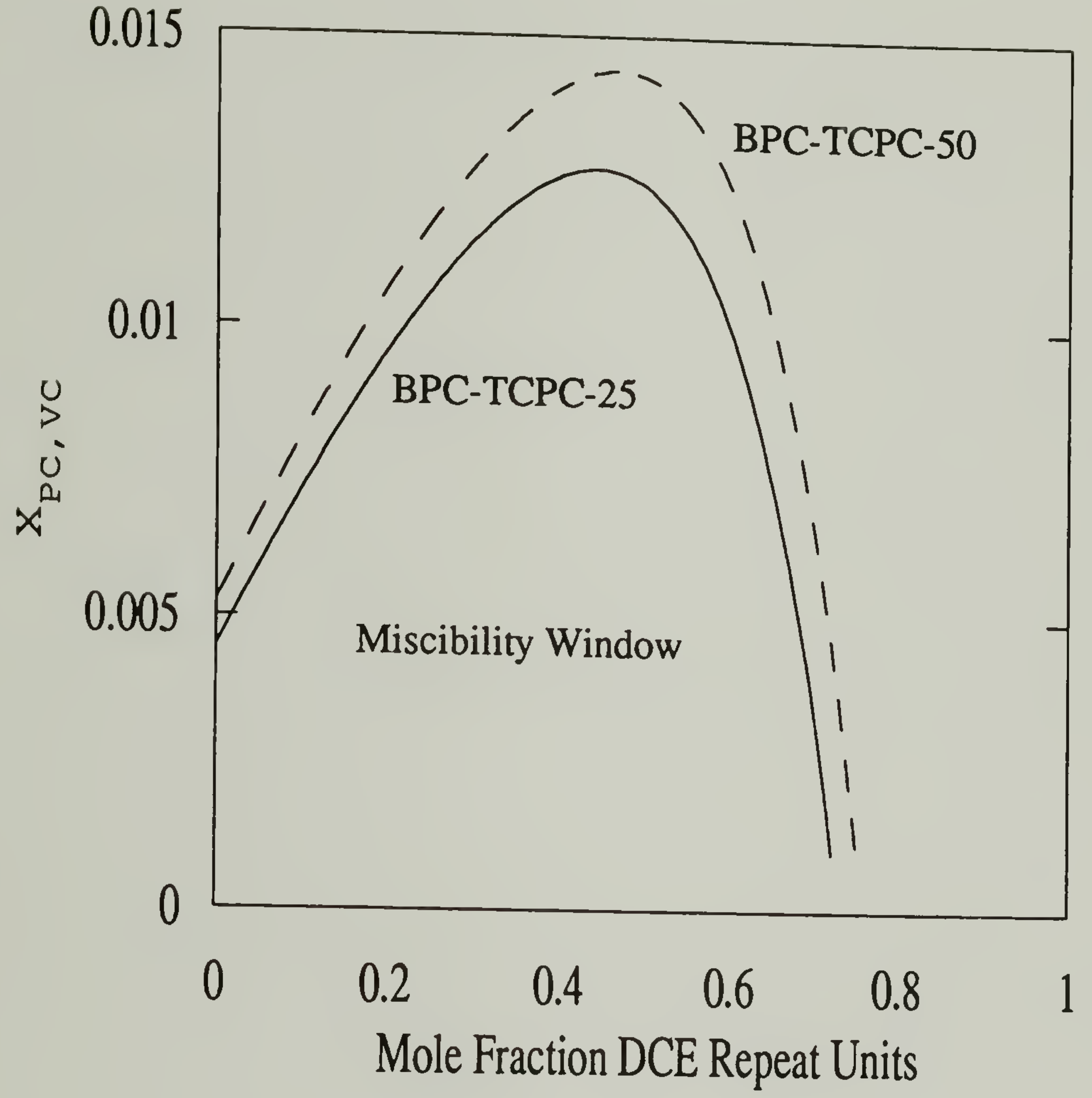

Figure 5.5. Effect of varying $X_{PC,VC}$ on miscibility window.

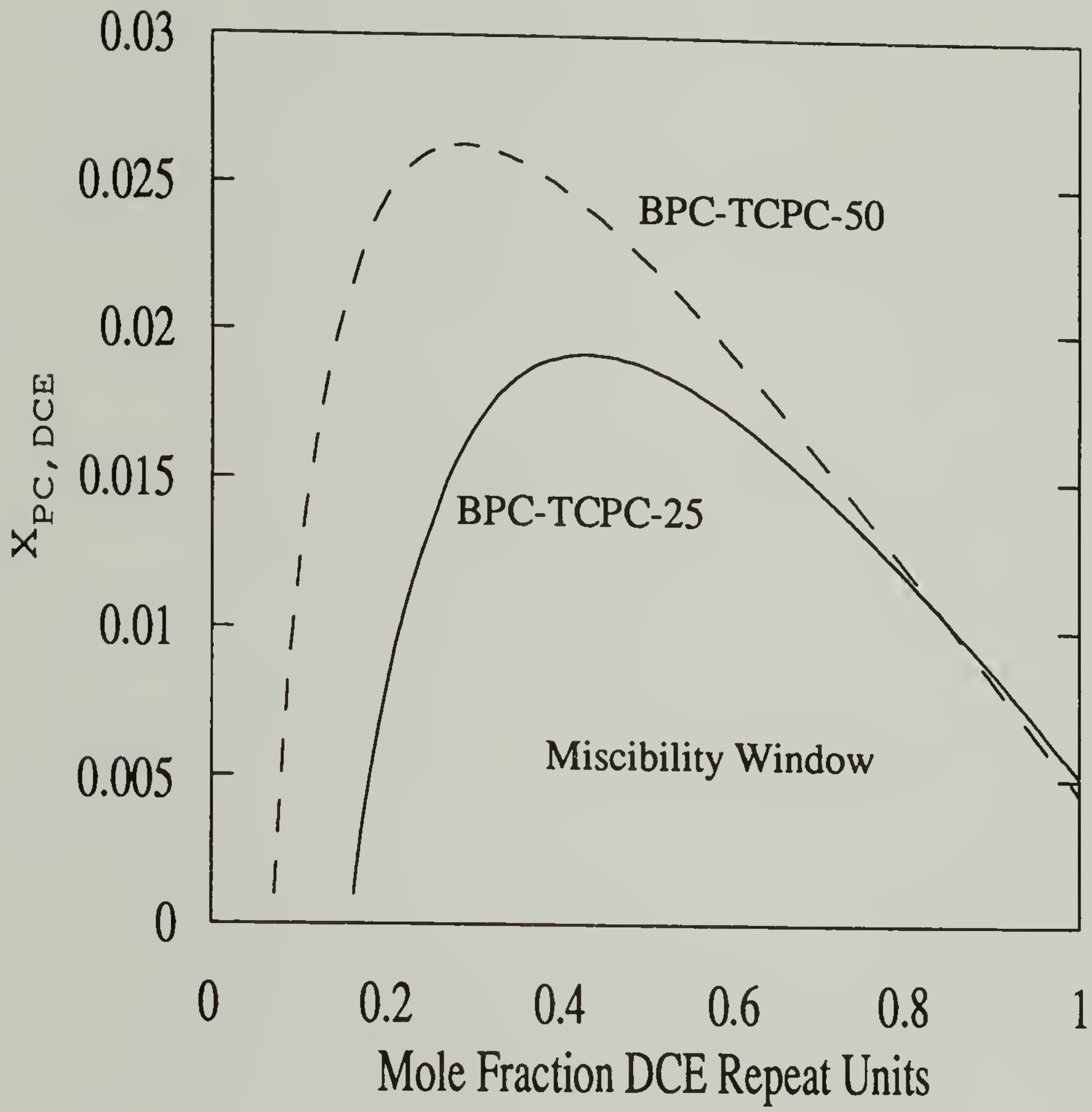

Figure 5.6. Effect of varying $X_{PC,DCE}$ on miscibility window.

(χ_{critical} in these blends is 0.005). The region of miscibility is seen to decrease as the $\chi_{\mathrm{PC,VC}}$ and $\chi_{\mathrm{PC,DCE}}$ are increased. Both $\chi_{\mathrm{BPC\text{-}TCPC\text{-}25,DCE}}$ and $\chi_{\mathrm{BPC\text{-}TCPC\text{-}25,VC}}$ calculated from the experimental window boundaries are within 0.003 of the limiting values for the formation of miscibility window. These figures illustrate the sensitivity of the miscibility window to subtle changes in χ_{ij}'s.

TMPC-TCPC Copolymers Blended with PVC and CPVCs

The TMPC-TCPC copolymer system is also one in which there is a positive interaction parameter between the repeat units. Because $\chi_{\mathrm{TMPC,TCPC}} > \chi_{\mathrm{BPC,TCPC}}$, it is expected that the effect of intramolecular repulsion will be greater in blends of TMPC-TCPC copolymers with PVC and CPVCs. This will affect the boundaries of the miscibility window.

It is seen that a larger composition range of TMPC-TCPC copolymers are miscible with PVC (Figure 5.7). The copolycarbonates form single-phase blends with PVC above a TCPC content of 41 mole %. This effect may be attributed to the large intramolecular effect within the TMPC-TCPC copolymer. A large positive value of $\chi_{\mathrm{TMPC,TCPC}}$ coupled with a negative or nearly zero value of $\chi_{\mathrm{TCPC,VC}}$ is needed to overcome the positive $\chi_{\mathrm{TMPC,VC}}$ and produce a negative χ_{blend}.

The TMPC-TCPC-41 shows a miscibility window in blends with solution-CPVCs similar to that seen in the BPC-TCPC-25

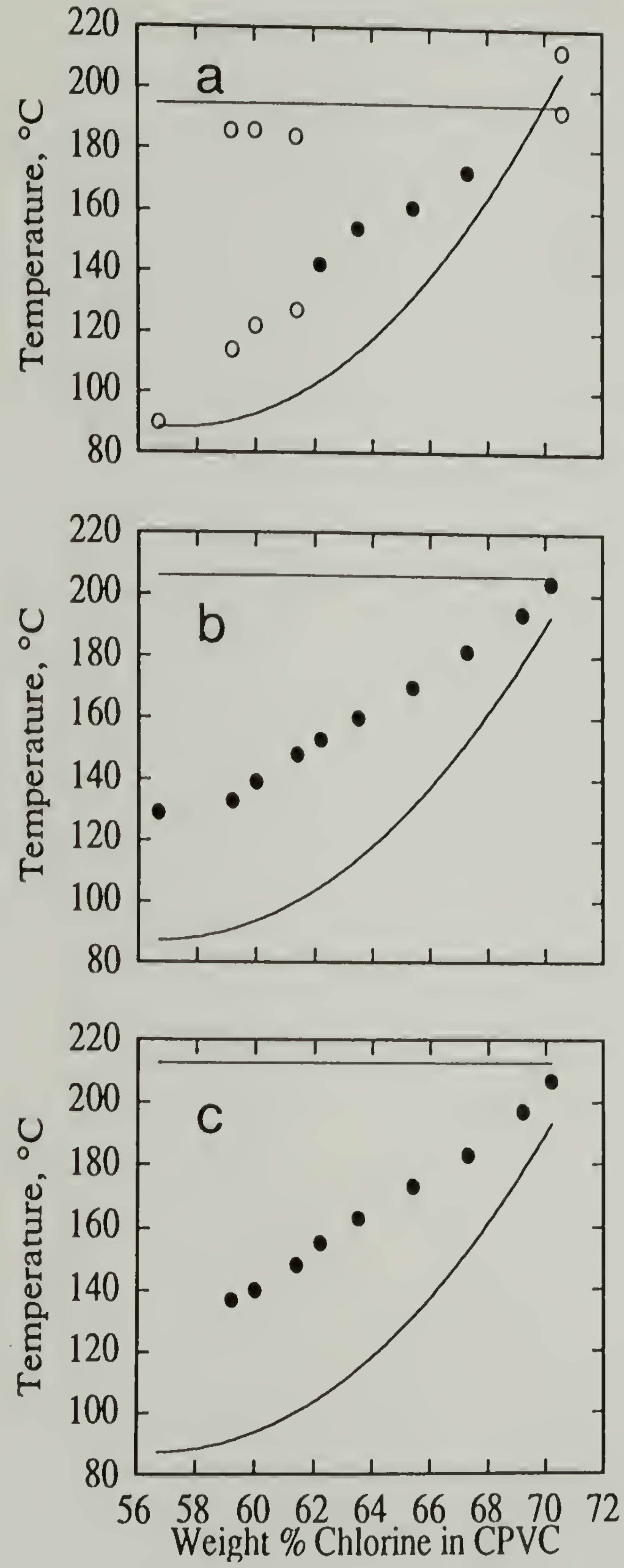

Figure 5.7. Glass transition temperature of 50/50 blends of TMPC-TCPC-copolymers with solution-CPVCs. (a) TMPC-TCPC-42; (b) TMPC-TCPC-58; (c) TMPC-TCPC-91.

blends. For the copolymers having TCPC contents greater than 41 mole %, miscibility is found in all CPVC blends (up to CPVC-11).

Like the BPC-TCPC copolymer/CPVC blends, raising the annealing temperature does not induce phase separation in miscible blends along the miscible-immiscible boundary. The temperature range for annealing experiments is further restricted in TMPC-TCPC-containing blends due to the higher glass transition temperatures of these copolycarbonates.

Solution-CPVCs Blended with HFPC-TMPC-50 and BPC-TBPC-50

Both HFPC/TMPC and BPC/TBPC homopolymer blends form two-phase binary mixtures. Copolymers derived from these monomer pairs, therefore, might form single phase blends with PVC and CPVCs if the repulsive, intramolecular interactions can overcome the unfavorable intermolecular interactions.

The T_g behavior of BPC-TBPC-50 blended with PVC is shown in Figure 5.8. The samples were cast from methylene chloride solution (4% w/v) and dried at 50^oC under a nitrogen stream. With the exception of the CPVC-8/(BPC-TBPC-50) blends, all the cast films were cloudy.

Opacity is considered an indication of immiscibility. Heating of these samples led to the formation of a single phase. The first heats in the calorimeter showed two glass transitions; the second heats, following annealing and quenching, had a single glass transition temperature. Two

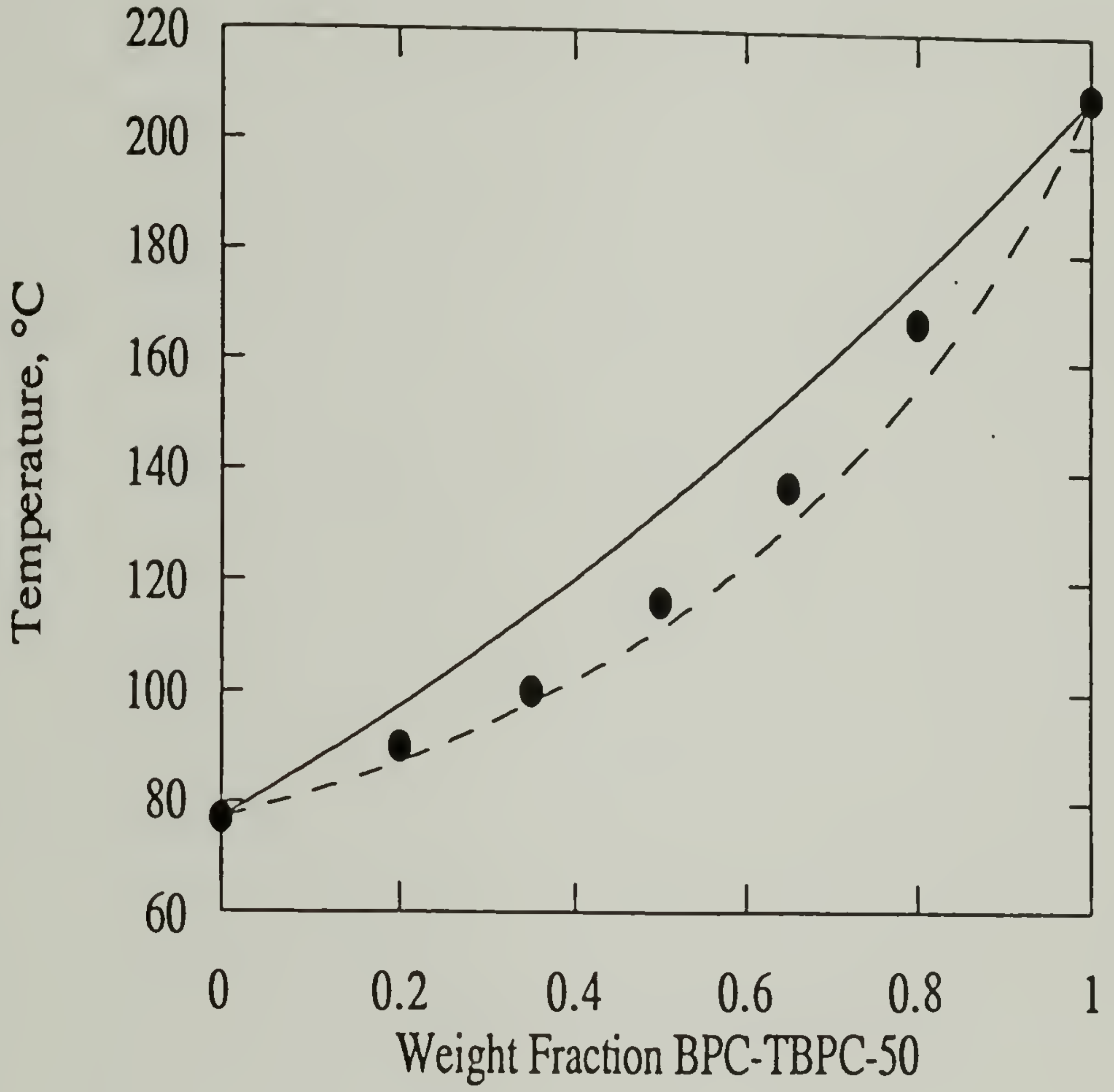

Figure 5.8. Glass transition temperature of BPC-TBPC-50/PVC blends. The solid and dashed curves represent predicted T_g's based of Equations (3-1) and (3-2), respectively.

explanations to account for this finding are the existence of a UCST (upper critical solution temperature) or a ΔX-effect (solvent interacts with one component more favorably, leading to phase separation of the polymers while in solution).[8] If a UCST exists, it would not be possible to determine the critical temperature, T_c, with great accuracy because of the high viscosity of the polymer mixture. UCST behavior is not frequently observed in high molecular weight polymer-polymer blends, so the ΔX-effect is probably the cause of film cloudiness. Upon heating, the phases intermix to achieve equilibrium. The single phase which results is characterized by a single, composition dependent glass transition temperature.

Blends of HFPC-TMPC-50 with PVC-0 and CPVC-5 were found to be immiscible in the blend composition range from 25% to 75% (by weight) polycarbonate copolymer. Samples were annealed in the DSC cell at 180°C and 200°C for 15 minutes. Though the cast samples were transparent, the component T_g's are not effected, and the incremental specific heat change at T_g for each component is proportional to composition. The transition breadth of each T_g is unaffected by blending, indicating that phase mixing is not occurring. The broad melt endotherm is present in the PVC blends, partially obscuring the copolycarbonate T_g. While the features of the polycarbonate T_g are difficult to obtain in the PVC blends, the PVC glass transition is unaffected by the presence of the higher T_g component.

Summary

It has been shown that copolymerization provides a means through which miscibility may be induced. In blends of solution-CPVCs with TCPC-containing copolymers, some of the interactions are attractive between the TCPC and vinyl chloride repeat units. Intramolecular effects also influence the phase behavior. The significance of the intramolecular copolymer effect was illustrated for BPC-TCPC copolymer/solution-CPVC blends; small changes in the magnitude of the VC-DCE interaction parameter were shown to lead to dramatic reduction in the width of the window of miscibility or disappearance of this window.

The copolymerization of BPC and TBPC gives a copolymer having a more attractive processing characteristics--lower glass transition temperature--than TBPC. This copolymer forms single phase blends with PVC and solution-chlorinated PVCs, a promising result considering that this PC is of very high molecular weight. BPC-TBPC repulsion within the copolymer contributes to the forces driving mixing.

In spite of its low molecular weight, HFPC-TMPC-50 did not form single phase blends with the solution-CPVCs. Various weight proportions were studied; all blends exhibited two glass transition temperatures. From the perspective of the mean field approach, the intermolecular repulsion overwhelms any favorable contribution from intramolecular effects. χ_{blend} is of sufficient magnitude to overcome the favorable contribution of the combinatorial terms (low molecular weight polycarbonate copolymer) to the free energy function.

In the next chapter, segmental interaction parameters, χ_{ij}'s, will be determined for the copolymer/copolymer blend systems investigated in this chapter.

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CHAPTER 6

ESTIMATION OF SEGMENTAL INTERACTION PARAMETERS FROM AB / CD BLENDS

In the previous two chapters, it has been shown that the miscibility of PVC and solution-CPVCs with polycarbonate copolymers is strongly dependent upon the composition of the copolycarbonate. Windows of miscibility exist for certain polycarbonate copolymers. In the case of TCPC-containing copolymers, this window increases as the TCPC-content increases, due in part to the miscibility of TCPC with PVC and most solution-CPVCs.

In the this chapter, data from the previous two chapters will be used to construct miscibility maps similar to that described for the hypothetical $A_{1-x}B_x$ /$C_{1-y}D_y$ system in Chapter 2. The two blend systems to be investigated will be the solution-CPVC/poly(BPC-*co*-TCPC) and solution-CPVC/ poly(TMPC-*co*-TCPC) blends. From the miscibility maps, it is possible to define a miscible region which can be analyzed by the mean field analysis.[1-3]

Solution-Chlorinated PVC / BPC-TCPC Copolymer Blends

The miscibility map for solution-CPVCs (modeled as vinyl chloride (VC)-1,2-vinylidene chloride (DCE) copolymers) blended with BPC-TCPC copolymers is shown in Figure 6.1. The region bounded by the elliptical curves is the single-phase, miscibility window. It is seen that the miscibility region occupies a significant region of the diagram. The miscibility behavior shown is for 50/50 blends (by weight). The map is considered an isothermal slice through a three-dimensional composition-composition-temperature diagram. "Composition" refers to the copolymer composition. Factors leading to this miscible region are favorable interactions between TCPC and PVC, and intramolecular, repulsive copolymer effects.

To use the mean field theory, the miscible/immiscible boundary needs to be defined mathematically. To accomplish this, a computer program was written; the program can be found in the Appendix. With this program, it was possible to place a conic section (an ellipse or hyperbola) anywhere on the diagram. Position, angle of orientation and the aspect ratio were user-defined. Fitting of the boundary was done by trial-and-error, and boundaries were chosen that best fit the miscible-immiscible boundary data. From the inputted information, the generalized quadratic function for the conic section was generated. Using the value of $\chi_{\mathrm{VC,DCE}}$ from Shiomi *et al.*[4], the equation was normalized, and values

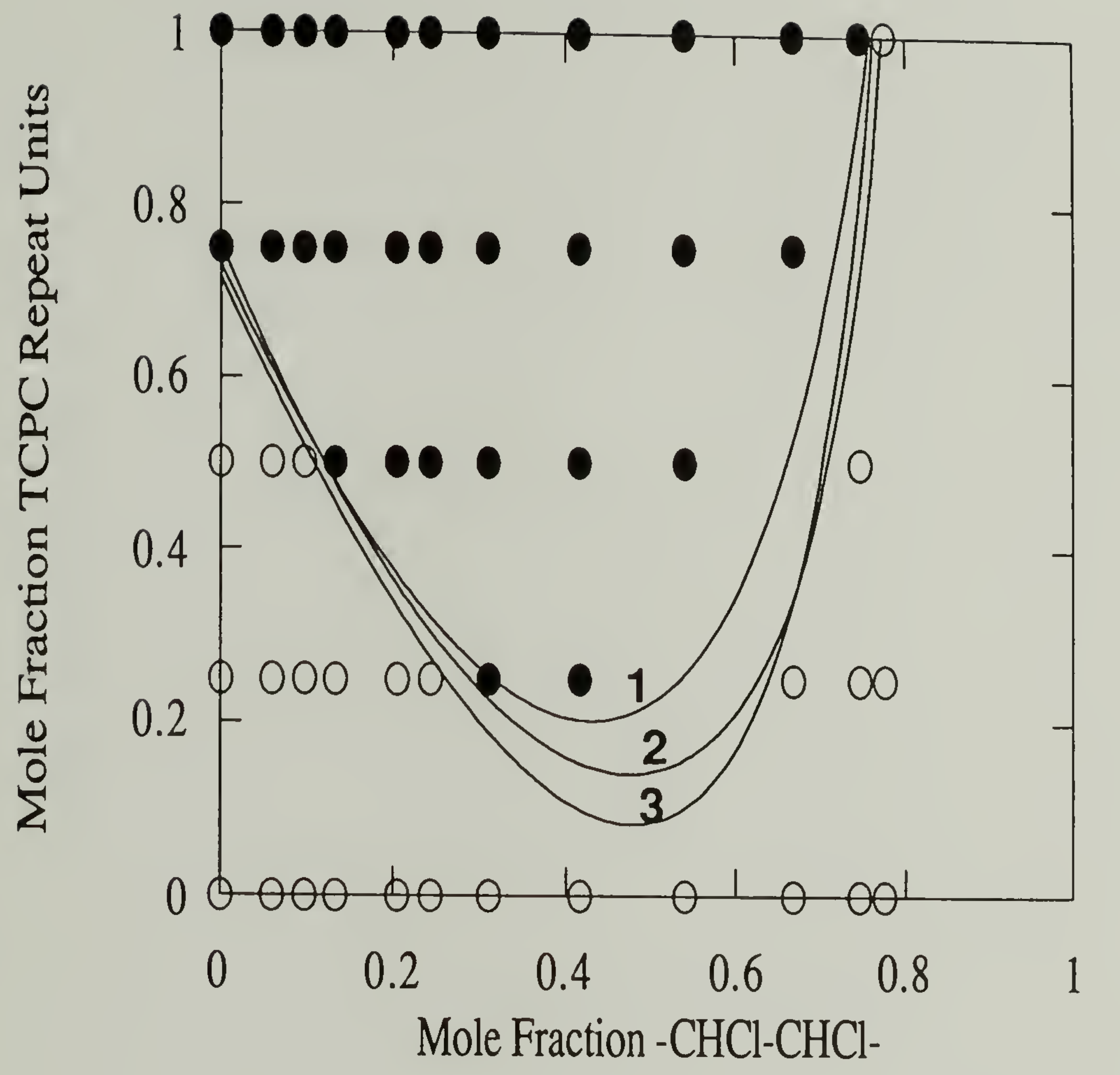

Figure 6.1. Isothermal, miscibility map for solution-CPVCs blended with BPC-TCPC copolymers. Blend composition is 50/50 by weight. Closed circles represent miscible blends; open circles are two-phase blends.

of the various segmental interaction parameters, X_{ij}'s, were determined from Equation (1.9).

Because of the wide spacings of copolymer compositions in the polycarbonates, a number of curves can be fit to the data. In Figure 6.1, some of the ellipses which closely fit the data are shown. The quadratic equation for each ellipse is

curve 1:

$$0.042x^2 + 0.012xy + 0.001y^2 - 0.039x - 0.016y + 0.011 = 0$$

curve 2:

$$0.042x^2 + 0.014xy + 0.004y^2 - 0.042x - 0.019y + 0.012 = 0$$

curve 3:

$$0.042x^2 + 0.015xy + 0.001y^2 - 0.042x - 0.016y + 0.011 = 0$$

The region of largest uncertainty is the PC copolymer composition range 0 to 25 mole % TCPC. Here, the miscible region may extend to PC copolymers with as low as 7 mole % TCPC. Because the X_{ij}'s are related to the coefficients of the quadratic equation for the conic section bounding the miscible region, each curve will generate a different set of X_{ij}'s. However, the change in any one X_{ij} is not obvious from the change in the ellipse, because the coefficients of the quadratic equation are linear combinations of X_{ij}'s.

To see how the X_{ij}'s vary with the boundary, the X_{ij}'s estimated for the three curves in Figure 6.1 are listed in Table 6.1. $X_{critical} = 0.004$, based on the molecular weight

Table 6.1. Comparison of interaction parameters for the VC-DCE / BPC-TCPC system estimated from the curves shown in Figure 6.1. $\chi_{\mathrm{critical}} = 0.004$ and $\chi_{\mathrm{VC,DCE}} = 0.042$ (after Shoimi *et al.*).

χ_{ij}	Curve 1	Curve 2	Curve 3
$\chi_{\mathrm{BPC,TCPC}}$	0.001	0.004	0.001
$\chi_{\mathrm{BPC,VC}}$	0.015	0.016	0.015
$\chi_{\mathrm{TCPC,VC}}$	0.000	0.001	0.000
$\chi_{\mathrm{BPC,DCE}}$	0.018	0.016	0.015
$\chi_{\mathrm{TCPC,DCE}}$	0.015	0.015	0.015

data of the PCs and CPVCs; the molar volume of a PVC repeat unit is used as a reference to correct for the size difference between PVC and PC repeat units. The only interaction parameter for which a trend can be seen is $\chi_{BPC,DCE}$, which decreases monotonically from 0.018 to 0.015 as the area of the miscibility window increases. While the changes in the χ_{ij}'s are small, they greatly affect the size of the miscible region. The number of acceptable boundaries is restricted by the close proximity of CPVC compositions on the left-hand side of the diagram, and by the TCPC ($y = 1$) boundary between CPVC-11 and CPVC-12.

To be noted in the values presented in Table 6.1 is the similarity of $\chi_{BPC,VC}$, $\chi_{BPC,DCE}$, and $\chi_{TCPC,DCE}$. Intuition might lead one to conclude that the corresponding miscibility/immiscibility boundary should be symmetrical with respect to the miscibility map. However, Equation (1.9) reveals that the relationships between the χ_{ij}'s and the coefficients of the quadratic equation forming the boundary are more complex.

The similarity of $\chi_{BPC,DCE}$ and $\chi_{TCPC,DCE}$ is expected to lead to a common boundary. If both BPC and TCPC behaved similarly in the their blends with CPVCs, this boundary would be located at approximately 0.76 mole fraction of DCE repeat units. This is shown in Figure 6.2, in which $\chi_{BPC,VC}$ has been set equal to $\chi_{TCPC,VC}$ and all other χ_{ij}'s are at their estimated values. It is seen that the miscibility boundary is nearly a straight line at $x = 0.076$. The slight

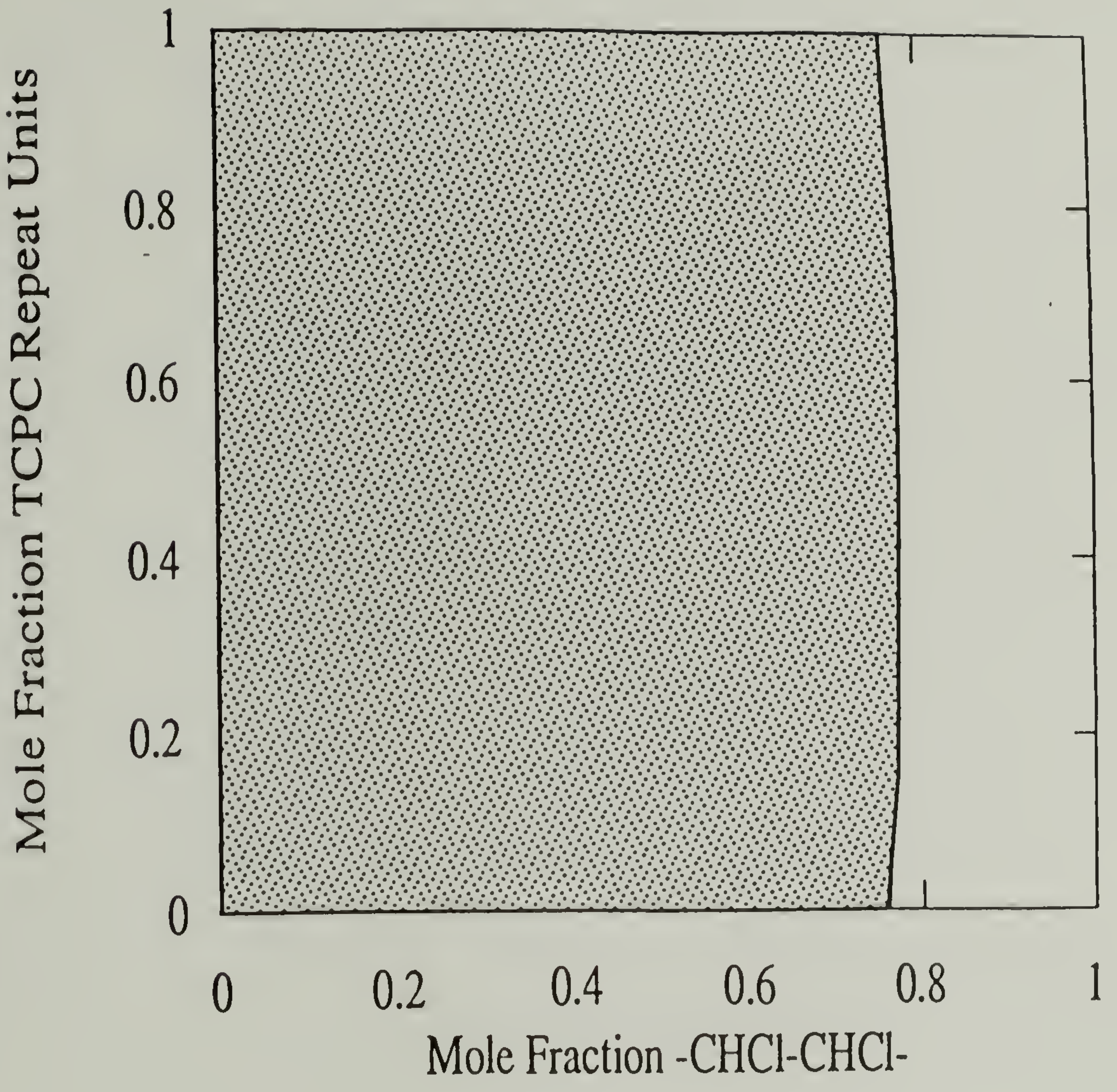

Figure 6.2. Miscibility map for solution-CPVC/BPC-TCPC copolymers if $\chi_{BPC,VC} = \chi_{TCPC,VC}$. Shaded area is single-phase, miscible region.

curvature outward at y = 0.5 is due the intramolecular repulsive effect within the polycarbonate copolymer.

The position of the minima of the miscible region on the miscibility map is sensitive to the values of $\chi_{BPC,TCPC}$, $\chi_{VC,DCE}$, and $\chi_{BPC,VC}$. The changes in the miscible/ immiscible boundary with these values is shown in Figure 6.3. Changes in these χ_{ij} are seen to affect the size of the miscibility window. When $\chi_{BPC,TCPC} < 0$, the conic section becomes hyperbolic (Figure 6.3a). Increasing $\chi_{VC,DCE}$ or decreasing $\chi_{BPC,VC}$ by 0.010 would lead to a window of miscibility in blends of BPC with some solution-CPVCs.

Figures 6.1 through 6.3 point out the complexities involved in this analysis, and demonstrate how "tuning" of the copolymer by proper selection of comonomers can greatly affect the blend behavior.

From the estimated χ_{ij}'s it is possible to calculate χ_{blend} as a function of copolymer composition. In Figure 6.4, χ_{blend} has been calculated for the poly(VC-*co*-DCE)/ poly(BPC-*co*-TCPC) system. As the mole fraction of TCPC units in the copolycarbonate increases from 0 to 1, χ_{blend} values decrease to values below the $\chi_{critical}$ (0.004). The locus of crossover points on the $\chi_{critical}$ line correspond to the miscible/immiscible boundary line shown in Figure 6.1.

In the preceding analysis, the use of mole fractions was used in the miscibility map. This notation is commonly

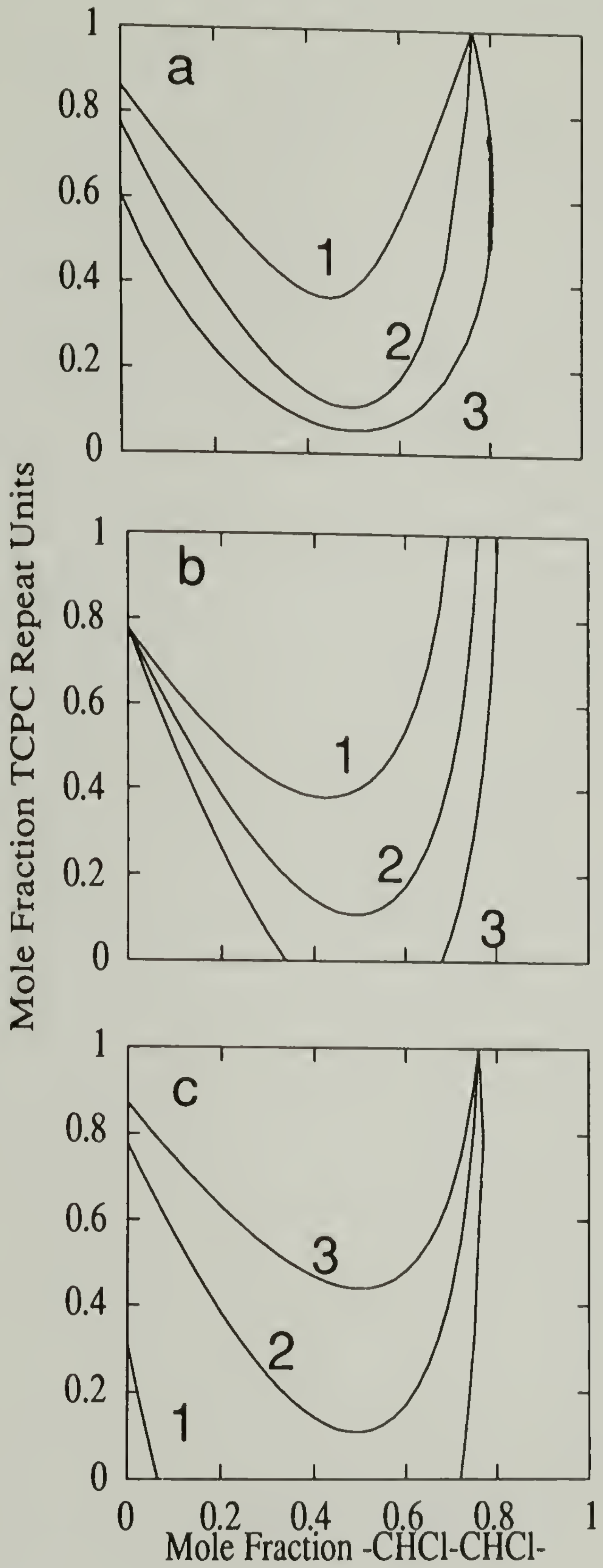

Figure 6.3. Effect on miscibility window as segmental interaction parameters are varied. (a) $\chi_{\mathrm{BPC,TCPC}}$ = (1) -0.008; (2) 0.002; (3) 0.010. (b) $\chi_{\mathrm{VC,DCE}}$ = (1) 0.032; (2) 0.042; (3) 0.052. (c) $\chi_{\mathrm{BPC,VC}}$ = (1) 0.006; (2) 0.016; (3) 0.026.

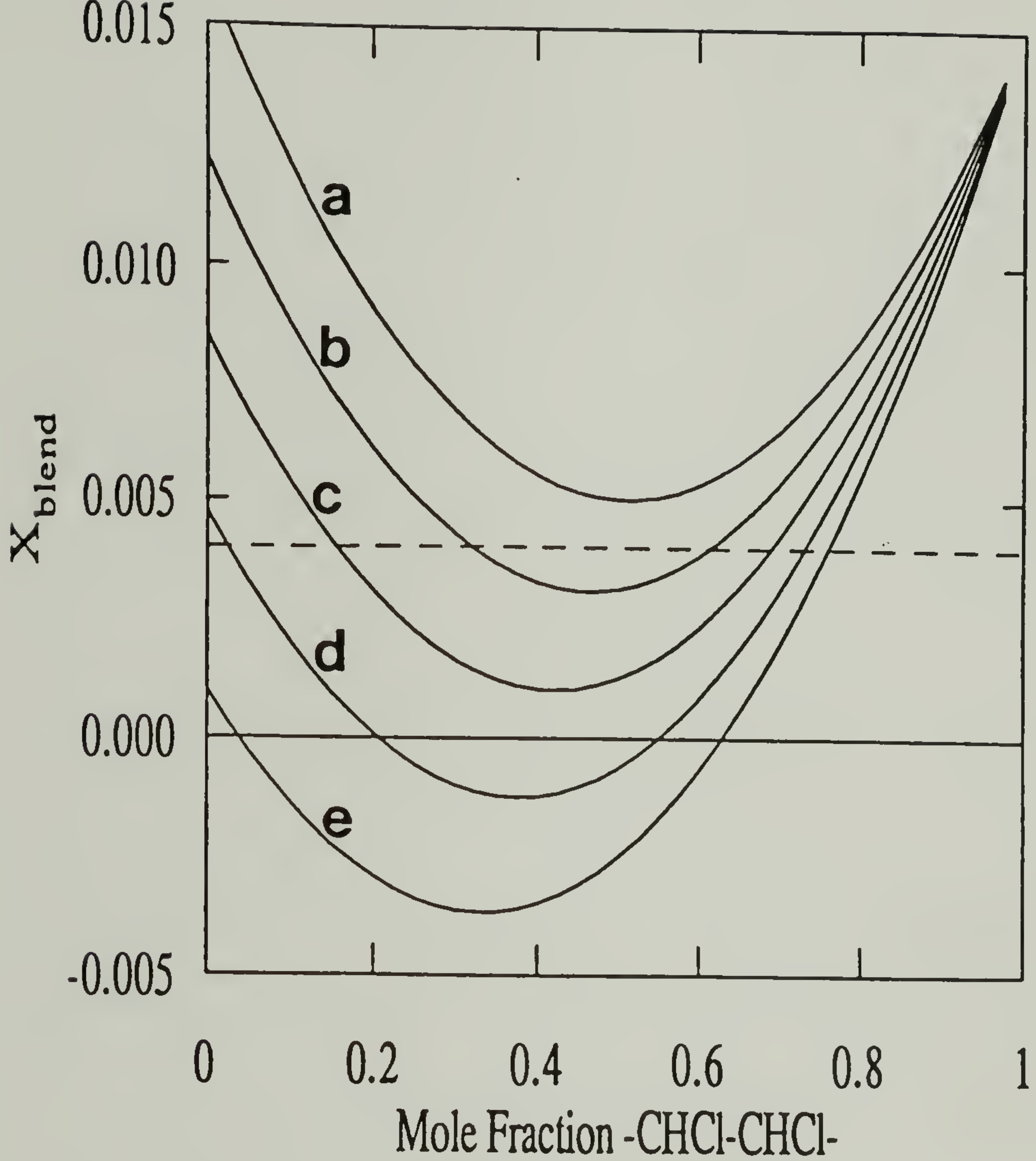

Figure 6.4. X_{blend} as a function of copolymer composition for VC-DCE/BPC-TCPC copolymer 50/50 blends. Values of y (the mole fraction of TCPC repeat units in the PC copolymer) are: a, 0.0; b, 0.25; c, 0.50; d, 0.75; e, 1.0. Dashed line is $X_{critical}$ (0.004).

used in the mean field theory treatment.[5-7] To be more accurate, however, the volume fraction should be used.[1,8,9] For comparison, the X_{ij}'s were calculated from volume fraction data, where the ordinate and abscissa correspond to the volume fractions of DCE repeat units and TCPC repeat units, respectively. Volume fractions of DCE and TCPC in the copolymers were determined using molar volumes calculated by a group contribution method described by Van Krevelen.[10] A comparison of X_{ij}'s is given in Table 6.2. It is seen that the choice of mole fraction or volume fraction does affect the X_{ij}'s, but only to a small extent.

Solution-Chlorinated PVC / TMPC-TCPC Copolymer Blends

The isothermal miscibility map for poly(VC-*co*-DCE)/poly(TMPC-*co*-TCPC) blends is shown in Figure 6.5. Unlike the poly(VC-*co*-DCE)/poly(BPC-*co*-TCPC) system, the boundary line between miscibility and immiscibility is severely restricted to a small number of elliptical boundaries. The miscible region does not extend to the TMPC-rich copolycarbonates. The interaction parameters $X_{TMPC,VC}$ and $X_{TMPC,DCE}$ might be expected to lead to this change in the boundary, and without carrying out any calculations, one may expect that $X_{TMPC,VC} > X_{BPC,VC}$ and $X_{TMPC,DCE} > X_{BPC,DCE}$. The right-hand portion of the single-phase region, where $x > 0.75$, is due to the intramolecular repulsion between the TMPC and TCPC repeat units. This observation leads to the conclusion that $X_{TMPC,TCPC}$ is greater than $X_{BPC,TCPC}$.

Table 6.2. Interaction parameters calculated from the mole fraction data and volume fraction data for the VC-DCE / BPC-TCPC blend system.

X_{ij}	mole fraction value	volume fraction value
$X_{BPC,TCPC}$	0.004	0.006
$X_{BPC,VC}$	0.016	0.021
$X_{TCPC,VC}$	0.001	0.001
$X_{BPC,DCE}$	0.016	0.016
$X_{TCPC,DCE}$	0.015	0.013

$X_{critical} = 0.004$ and $X_{VC,DCE} = 0.042$.

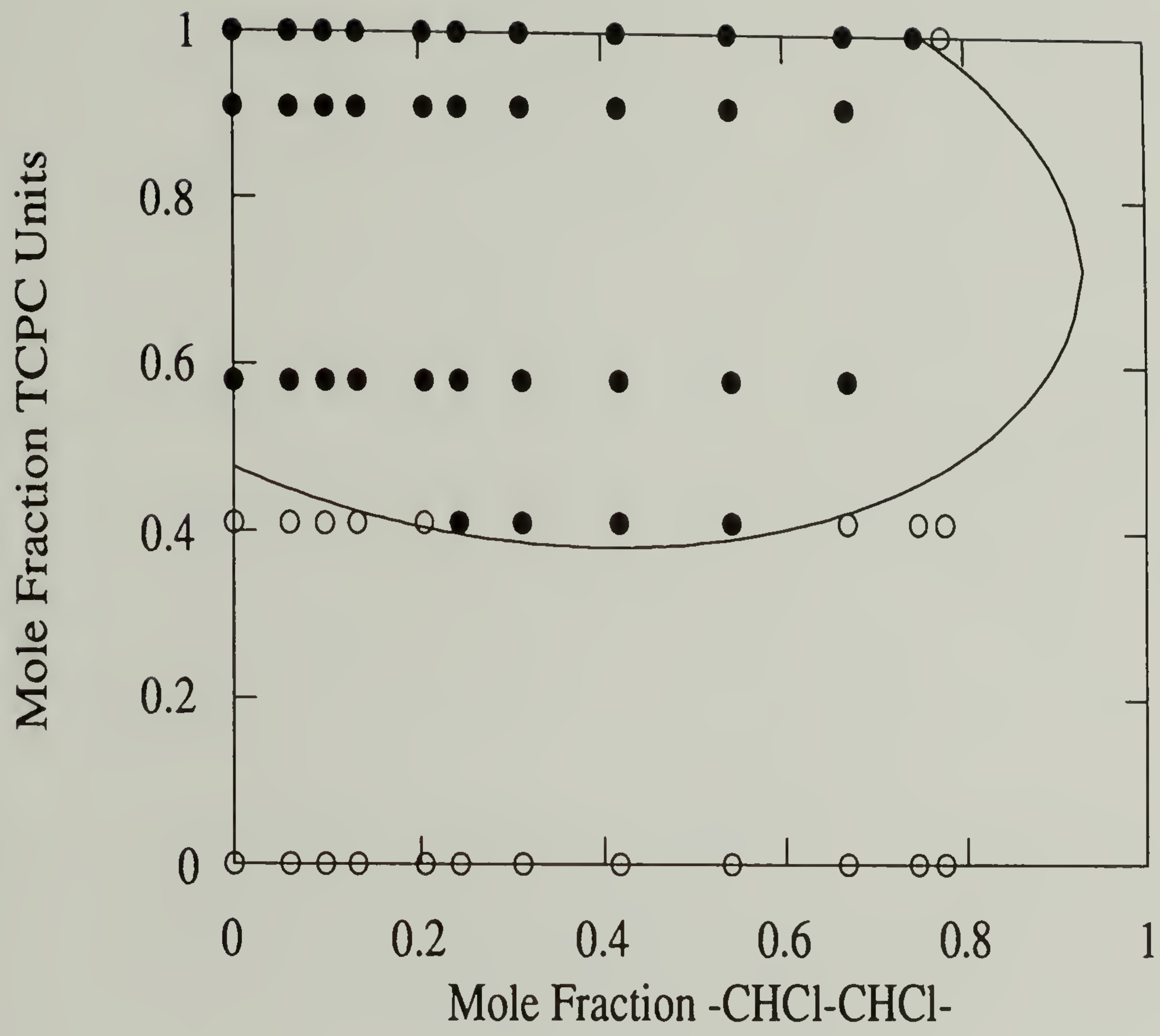

Figure 6.5. Isothermal, miscibility map for VC-DCE/ TMPC-TCPC copolymer blends. Filled circles represent miscible blends. Blend composition is 50/50 by weight.

The quadratic function shown in Figure 6.5 which bounds the miscible region is

$$2.858x^2 + 1.143xy + 6.845y^2 - 2.779x - 10.871y + 3.628 = 0 \quad (6.1).$$

This is normalized using A = $\chi_{VC,DCE}$ = 0.042 to give

$$0.042x^2 + 0.017xy + 0.101y^2 - 0.041x - 0.160y + 0.053 = 0 \quad (6.2).$$

From these coefficients and using $\chi_{critical}$ = 0.005 (from volume corrected degrees of polymerization based upon the molar volume of a vinyl chloride repeat unit) the five remaining χ_{ij}'s are calculated. The results are given in Table 6.3. Included in this Table are values based upon volume fractions, rather than mole fractions, on the ordinate and abscissa. If volume fraction is used, the normalized equation for the miscible-immiscible boundary is

$$0.042x^2 + 0.018xy + 0.105y^2 - 0.046x - 0.169y + 0.059 = 0 \quad (6.3).$$

As in the BPC-TCPC-containing blends, the differences between χ_{ij}'s using mole fraction and volume fraction are small. As predicted, the estimated values of $\chi_{TMPC,VC}$ and $\chi_{TMPC,DCE}$ are greater than their counterpart in the BPC-TCPC copolymer system. The intramolecular effect of $\chi_{TMPC,TCPC}$ can be noted by changing its value holding the other χ_{ij} constant. If $\chi_{TMPC,TCPC}$ is decreased by 0.010, the

Table 6.3. Segmental interaction parameters calculated for the VC-DCE / TMPC-TCPC blend system from miscibility map boundary. Values are calculated based on mole fractions (shown in Figure 6.5) and volume fractions (figure not shown). $\chi_{\mathrm{critical}} = 0.005$; $\chi_{\mathrm{VC,DCE}} = 0.042$.

χ_{ij}	mole fraction value	volume fraction value
$\chi_{\mathrm{TMPC,TCPC}}$	0.101	0.105
$\chi_{\mathrm{TMPC,VC}}$	0.058	0.064
$\chi_{\mathrm{TCPC,VC}}$	0.000	0.001
$\chi_{\mathrm{TMPC,DCE}}$	0.059	0.060
$\chi_{\mathrm{TCPC,DCE}}$	0.018	0.015

miscible-immiscible boundary along x = 0 increases above 0.5 mole fraction TCPC repeat units, decreasing the area of the miscibility window.

χ_{blend} as a function of VC-DCE copolymer composition is plotted in Figure 6.6. For each PC copolymer, the locus of points at which χ_{blend} crosses $\chi_{critical}$ forms the boundary seen in Figure 6.5. For a blend of infinite molecular weight components, for which $\chi_{critical} = 0$, the miscibility region would contract significantly.

Comparison of Calculated χ_{ij}'s

One of the objectives of this investigation was to determine the self-consistency of the mean field theory. In the blends studied, several χ_{ij}'s are determined in different fashions, allowing for comparison.

The two blend systems considered in this chapter have two χ_{ij}'s in common, $\chi_{TCPC,VC}$ and $\chi_{TCPC,DCE}$. In Tables 6.1 and 6.3, these values are seen to agree well with one another. This result is expected because the blend phase behavior on both miscibility maps at y = 1 (TCPC) is identical.

The PC interaction parameters $\chi_{BPC,TCPC}$ and $\chi_{TMPC,TCPC}$, were estimated in Chapter 3. Correcting for PC and VC repeat unit size differences, the values of these two parameters from Chapter 3 are $0.008 < \chi_{BPC,TCPC} < 0.014$ (at $265^{o}C$) and $0.033 < \chi_{TMPC,TCPC} < 0.052$ (at $250^{o}C$). The agreement among these values is not good. At first glance

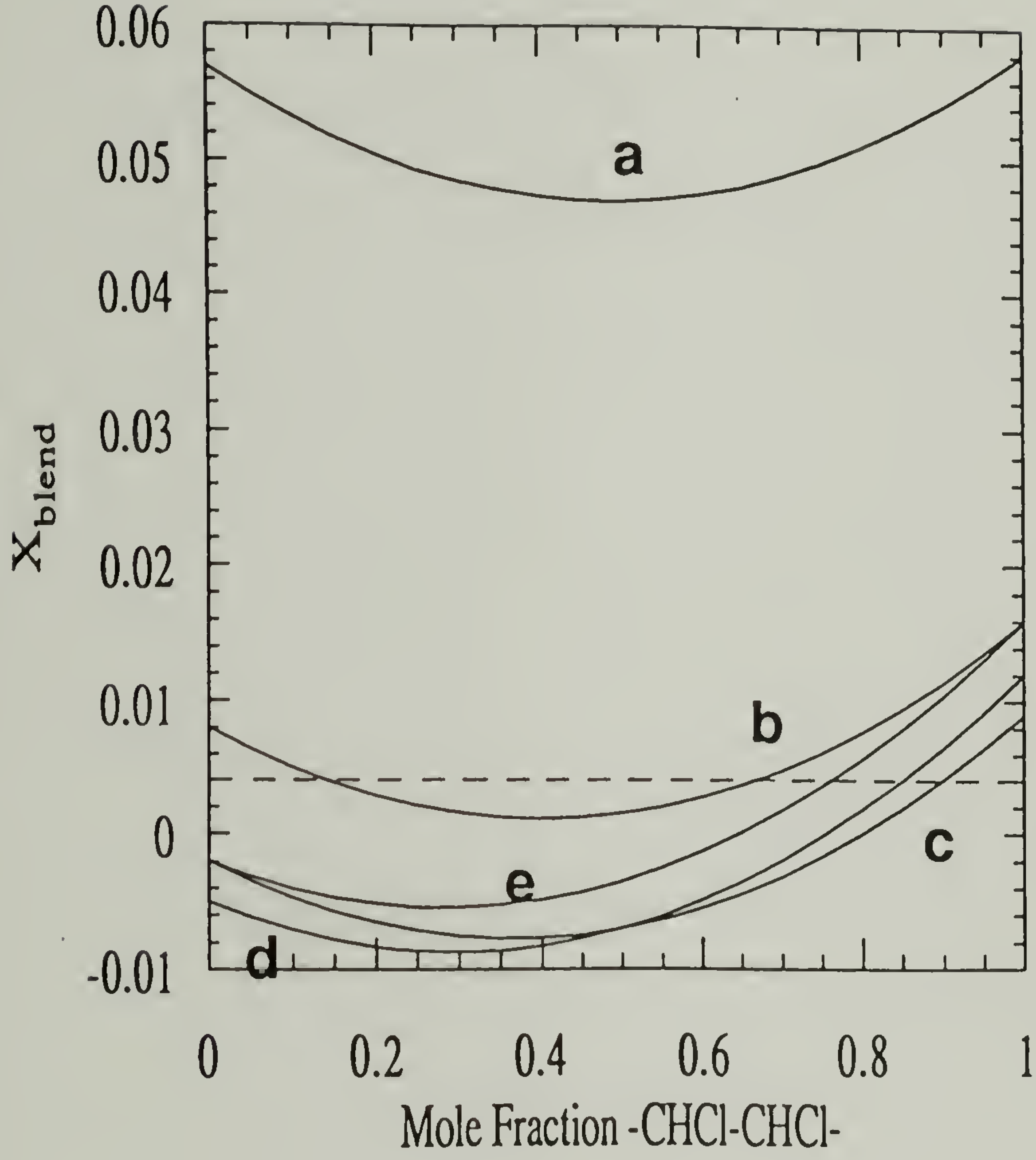

Figure 6.6. χ_{blend} as a function of copolymer composition for VC-DCE/TMPC-TCPC copolymer 50/50 blends. Values of y (the mole fraction of TCPC repeat units in the PC copolymer) are: a, 0.0; b, 0.41; c, 0.58; d, 0.91; e, 1.0. Dashed line is $\chi_{critical}$.

this may appear to cast doubt on the mean field theory as a means to determine interaction parameters. However, some factors need mentioning which can explain the discrepancy in χ_{ij}'s.

The mean field treatment ignores the composition dependence of χ_{ij}. This is an important factor when considering the interaction of a PC repeat unit with either another PC repeat unit or a vinyl chloride-sized repeat unit. Because interacting surface areas change with composition due to the difference in size of the comonomers, this is expected to lead to some difficulties when attempting to compare the same χ_{ij} from different copolymer blend systems.[5] This may be the most significant factor explaining the difference in the calculated segmental interaction parameters. The calculated polycarbonate χ_{ij}'s are "effective" segmental interaction parameters, because the PC repeat units size is considered to be equal to that of a vinyl chloride repeat unit.

Temperature dependence of χ_{ij} is another explanation for the differences in $\chi_{BPC,TCPC}$ and $\chi_{TMPC,TCPC}$. When considering enthalpic and free volume effects on χ_{ij} as a function of temperature, two possible paths exist for χ_{ij} versus temperature (curves 1 and 2, Figure 6.7). The enthalpic contribution to χ_{ij} approaches zero as temperature is increased (curves 3 and 4). This effect leads to UCST behavior for systems in which χ_{ij} is positive (unfavorable to mixing). The entropic, or free volume, contribution

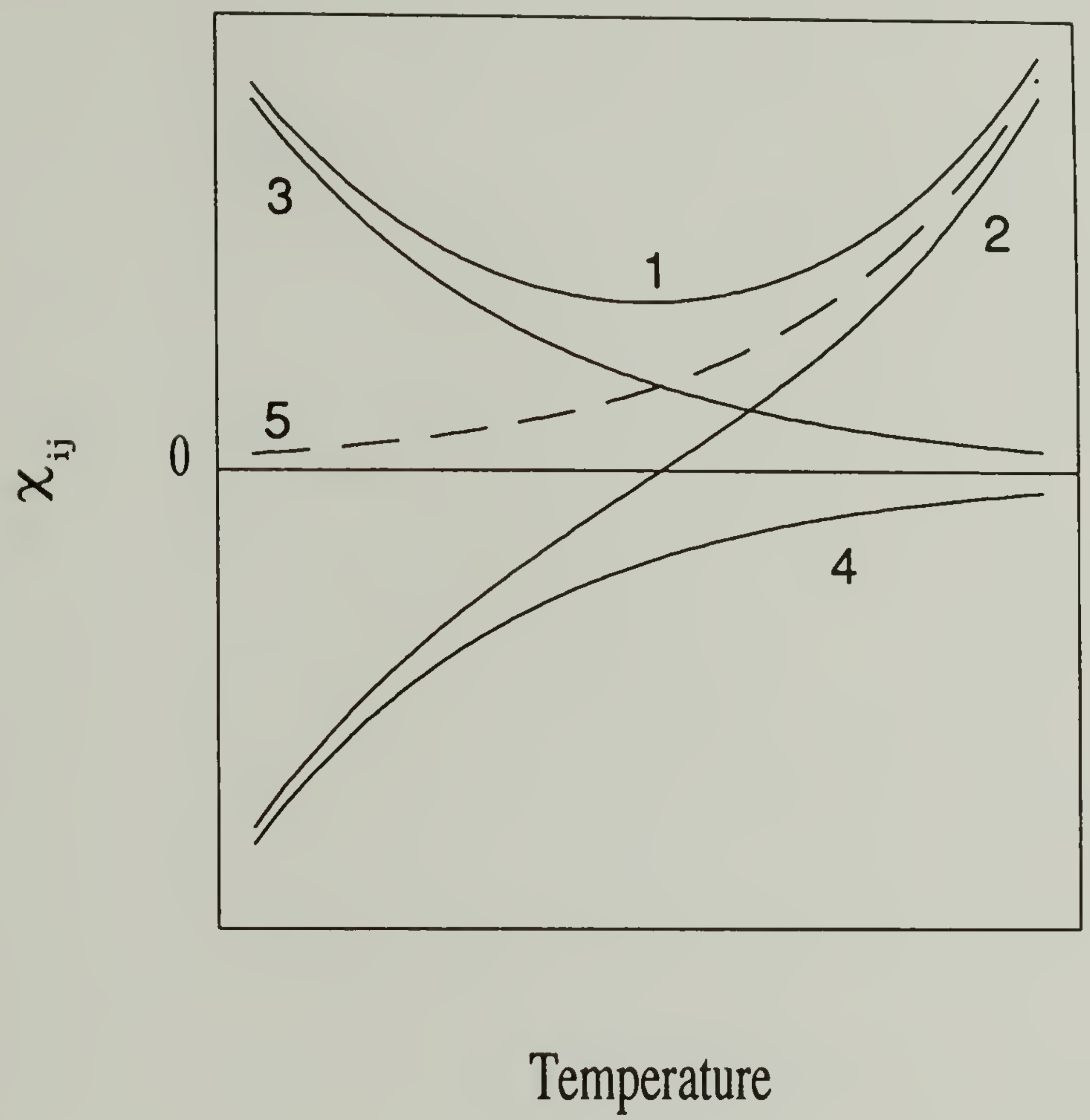

Figure 6.7. Contribution to X_{ij} (curves 1 and 2) from $X_{\mathrm{enthalpic}}$ (curves 3 and 4) and X_{entropic} (curve 5).

(curve 5) is always positive and increases with increasing temperature.[11] In a blend system with a favorable enthalpic contribution to X_{ij} ($X_{enthalpic} < 0$), the added free volume term will increase X_{ij} above zero (or $X_{critical}$ for polymers of finite molecular weight), resulting in LCST behavior (curve 2).

The effect of temperature is certainly a factor in this study. The annealing temperatures for the PC/PC blends were typically greater than 250°C; all annealing temperatures used in the CPVC/PC blends were below 240°C. The behavior of $X_{BPC,TCPC}$ could be following either curve 1 or 2 of Figure 6.7. The increase of $X_{BPC,TCPC}$ with temperature is indicative of a system which exhibits an LCST. The decrease of $X_{TMPC,TCPC}$ with increasing temperature fits the criteria of curve 1 in Figure 6.7. This blend system may or may not exhibit a UCST and an LCST; this occurrences would be dependent upon $X_{TMPC,TCPC}$ crossing $X_{critical}$. From experimental evidence, $X_{TMPC,TCPC}$ does not cross $X_{critical}$, and TMPC-TCPC are immiscible at all temperatures.

Summary

The mean field treatment has been used to determine segmental interaction parameters from blends of polycarbonate copolymers with solution-chlorinated PVCs (modeled as poly(vinyl chloride-*co*-1,2-dichloroethylene)). The estimated parameters are consistent with X_{ij}'s calculated from different copolymer systems.

The miscibility region exhibited by TMPC-TCPC and BPC-TCPC copolymers blended with solution-CPVC is created in large part by the intramolecular repulsion within each copolymer. Because $\chi_{TMPC,TCPC} > \chi_{BPC,TCPC}$, the miscibility region in TMPC-TCPC copolymer system is larger. The primary force creating the miscibility window in the BPC-TCPC copolymer system is the VC-DCE repulsion; $\chi_{BPC,TCPC}$ does influence miscibility, but its contribution is not as great. In the TMPC-TCPC-containing blends, the intramolecular repulsion within the polycarbonate copolymer is an important factor for the formation of the miscibility window.

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CHAPTER 7

CONCLUSION

Blends of polycarbonates with PVC and chlorinated PVCs (CPVCs) have been investigated. Using a mean field theory, binary segmental interaction parameters were determined in those blend systems containing copolymers.

In addition to polycarbonate/CPVC blends, binary polycarbonate blends were also studied. Interaction parameters were calculated for these systems from homopolymer/copolymer data. Investigations of polycarbonate/polycarbonate homopolymer blends provided information about the potential of a monomer pair to create a favorable intramolecular repulsion effect when copolymerized.

Summary

The investigation of polycarbonate/polycarbonate blends was of importance in this study. The results provide information regarding the strength of interaction between monomer segments. This is an important consideration when it is desirable to use a repulsive, copolymer effect to induce miscibility. The presence or lack of interaction will be reflected in the phase behavior of the materials. In this work, it was found that BPC and TCPC are miscible at temperatures exceeding 250°C, provided the polymers are of low molecular weight and the blend composition is not in the vicinity of the critical composition (approximately 50/50 by weight). The BPC/TMPC pair is miscible, and the remaining polycarbonate pairs form immiscible blends over the composition range 20-80% by weight. Lowering the molecular weight of one or both components does not lead to miscibility in these blends.

TCPC was shown to be miscible with PVC, and CPVCs having chlorine contents up to 70.2% by weight. The behavior of TCPC in its blends with the solution-CPVCs can be explained by considering that miscibility is due to two effects: a favorable interaction with vinyl chloride repeat units and an intramolecular repulsive effect within the solution-CPVC between vinyl chloride and 1,2-dichloroethylene repeat units.

Certain polycarbonate copolymers, such as BPC-TCPC-25 and TMPC-TCPC-41, formed single-phase blends with some solution-CPVCs, even though these copolycarbonate were immiscible with PVC and more highly-chlorinated solution-CPVCs. These "miscibility windows" provided further evidence of a copolymer effect driving miscibility.

The miscibility-immiscibility boundaries of copolycarbonate/solution-CPVC blends were used to determine segmental interaction parameters. Using a mean field theory developed to explain miscibility behavior in copolymer-containing systems, interaction parameters were calculated from polycarbonate/polycarbonate and polycarbonate/solution-CPVC systems. Estimated values were consistent with the observed blend phase behavior.

Suggestions for Future Studies

Quantities of material in this investigation were limited. Blends were solvent-cast or precipitated in small quantities (less than 0.5 g) to conserve polymer. Larger quantities of polycarbonate and solution-CPVCs would be useful so that samples could be processed in a manner similar to that used for PVC compounds, for example, mixing in an extruder at elevated temperature. The effect of miscibility on processing could be investigated. Also, the effects of thermal stabilizers and processing aids (e. g., lubricants, plasticizers) could be evaluated.

An investigation of the P-V-T behavior of TCPC would be of interest because of this polymers miscibility with PVC. In equation-of-state theories, matching of the thermal expansion coefficient may lead to miscibility. Using the mean field treatment, the interaction parameter for this system is very small and positive; similarity of TCPC and PVC P-V-T behavior could provide an explanation for miscibility.

There are many more aromatic polycarbonates which can be synthesized from bisphenol-A derivatives. Many of these materials have T_g's below 200°C. It might be expected that some homopolymers and/or copolymers derived from these materials will be miscible with PVC and CPVCs. Keeping the polycarbonate glass transition temperature relatively low would limit the need to anneal or process samples at temperatures close to the PVC degradation limit.

APPENDIX A

FT-IR SPECTRA OF POLYCARBONATE HOMOPOLYMERS

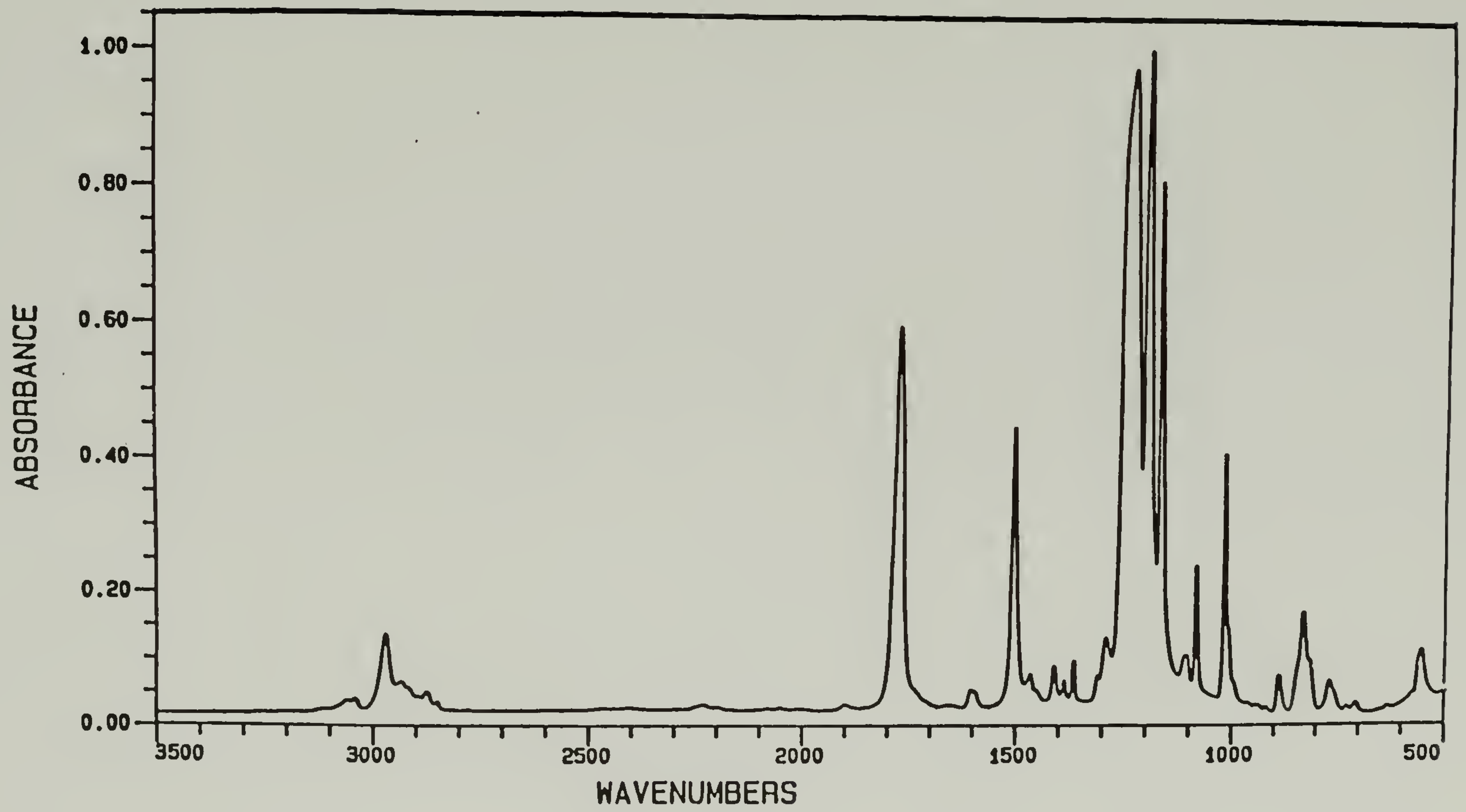

Figure A.1. FT-IR spectrum of bisphenol-A polycarbonate (BPC).

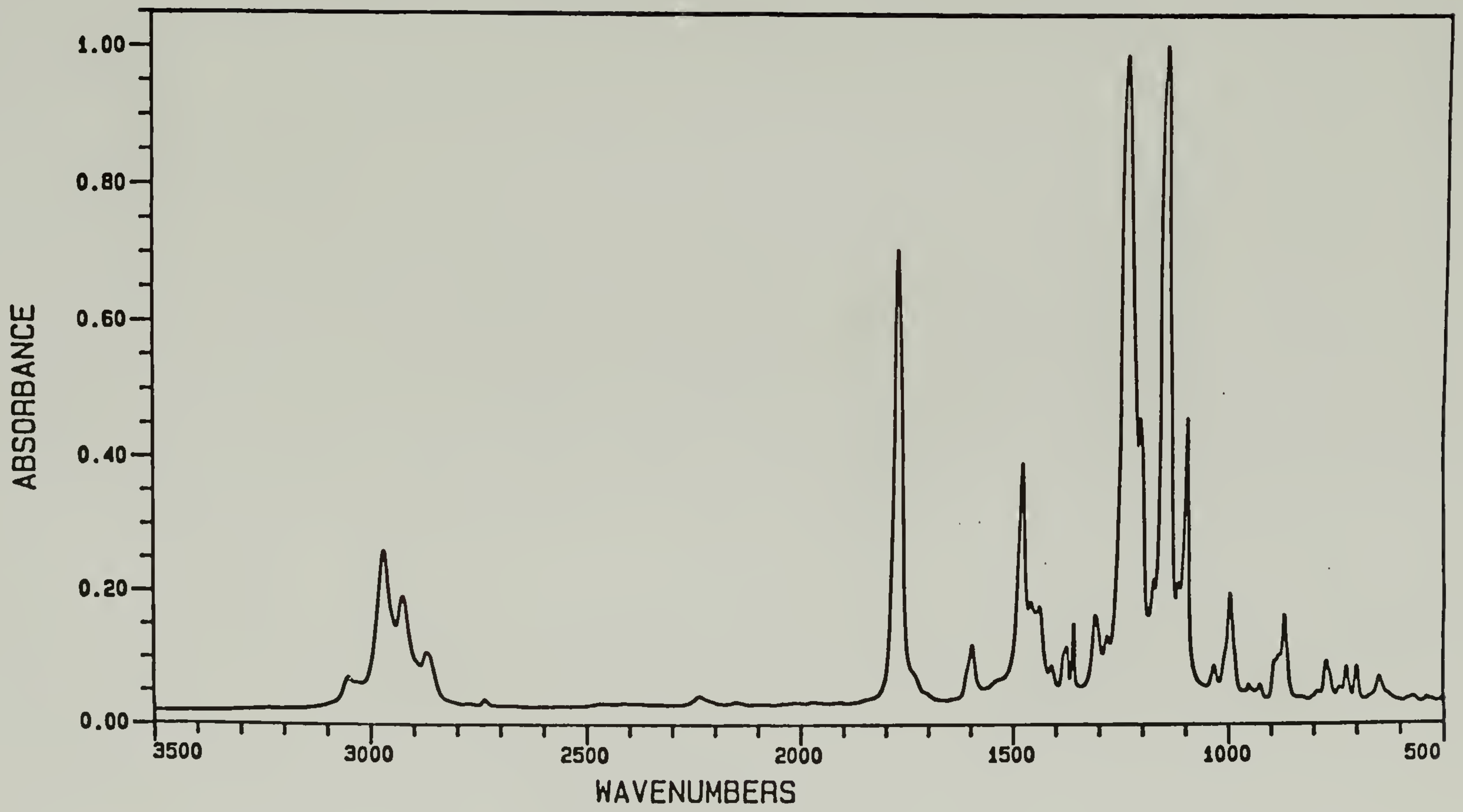

Figure A.2. FT-IR spectrum of tetramethylbisphenol-A polycarbonate (TMPC).

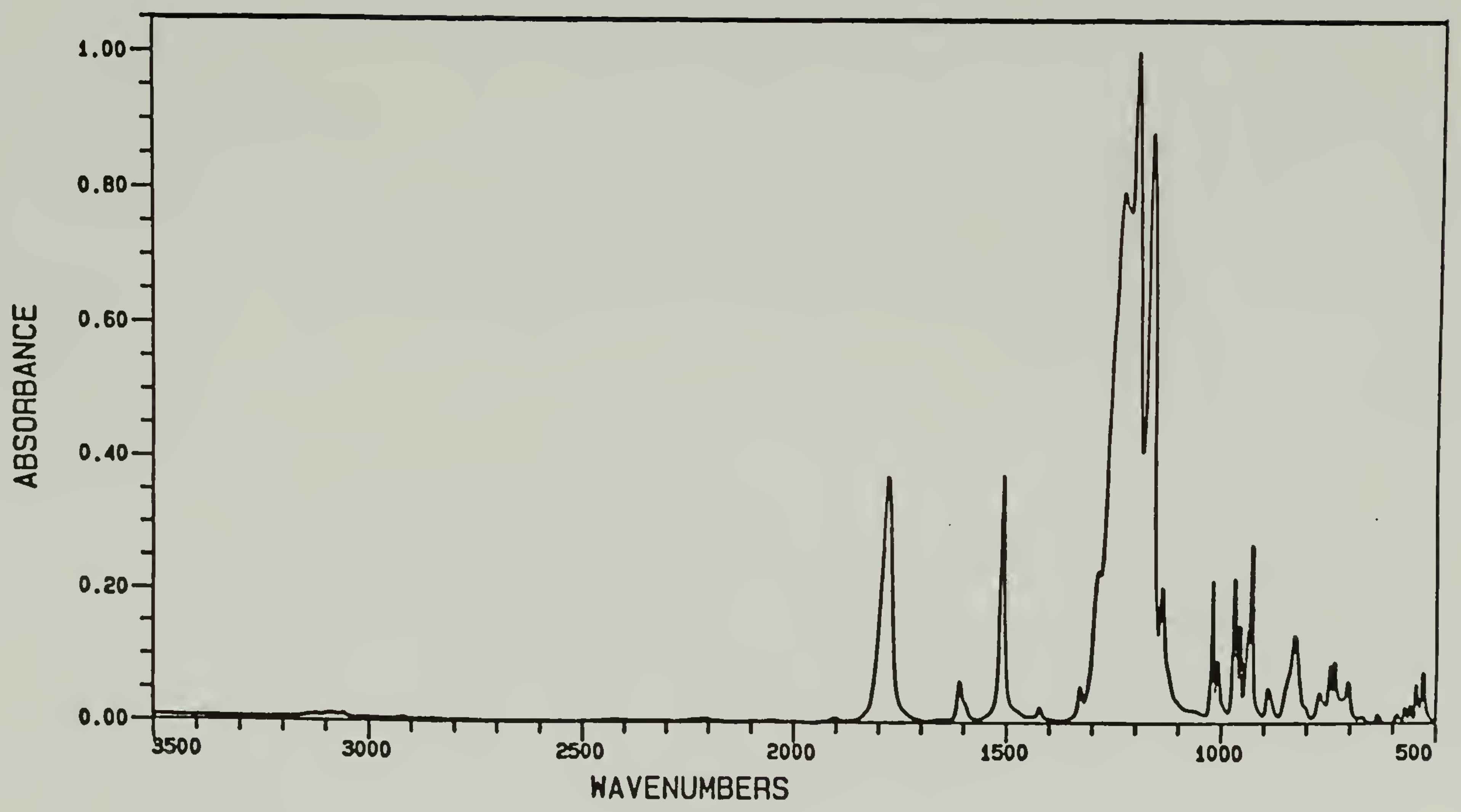

Figure A.3. FT-IR spectrum of hexafluorobisphenol-A polycarbonate (HFPC).

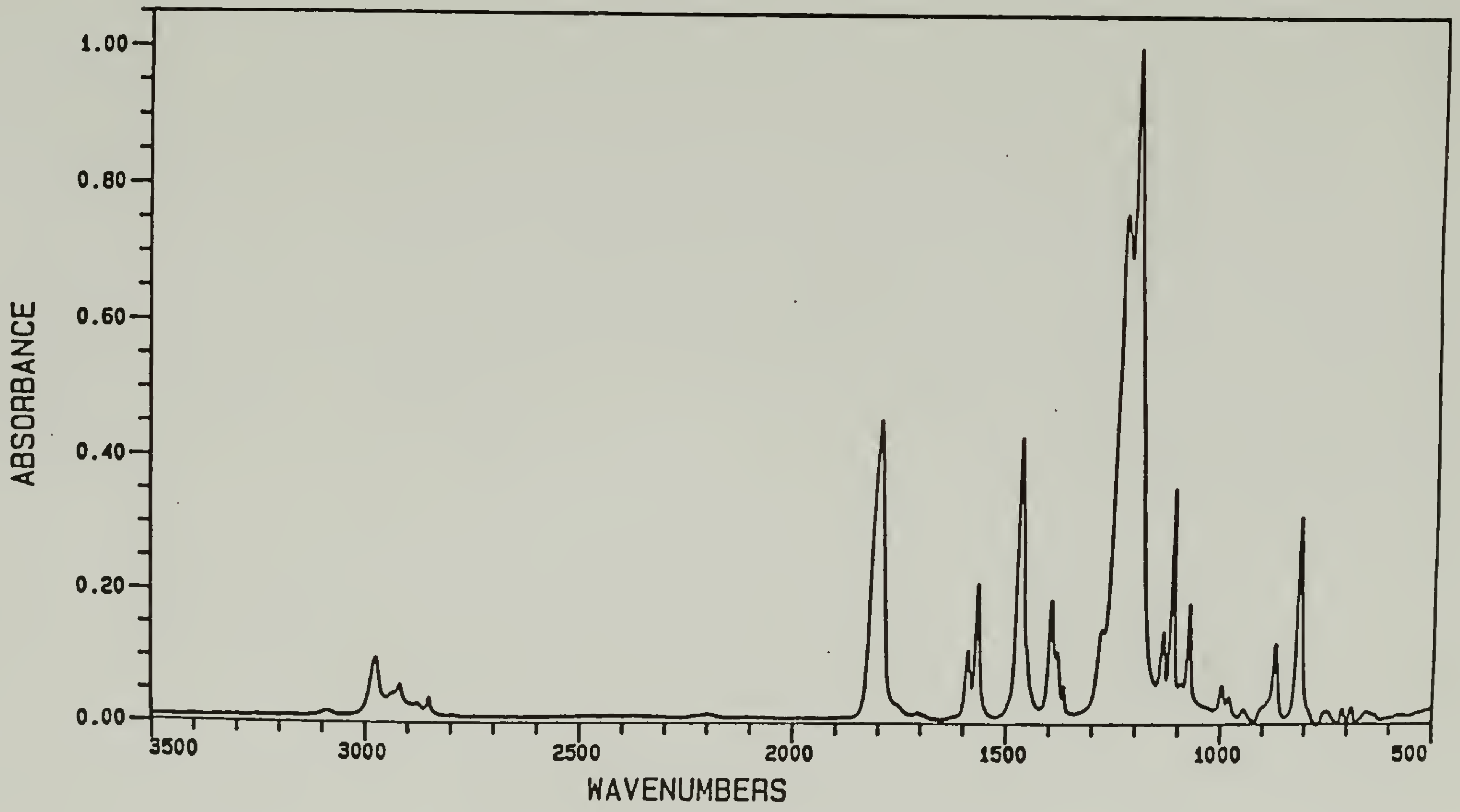

Figure A.4. FT-IR spectrum of tetrachlorobisphenol-A polycarbonate (TCPC).

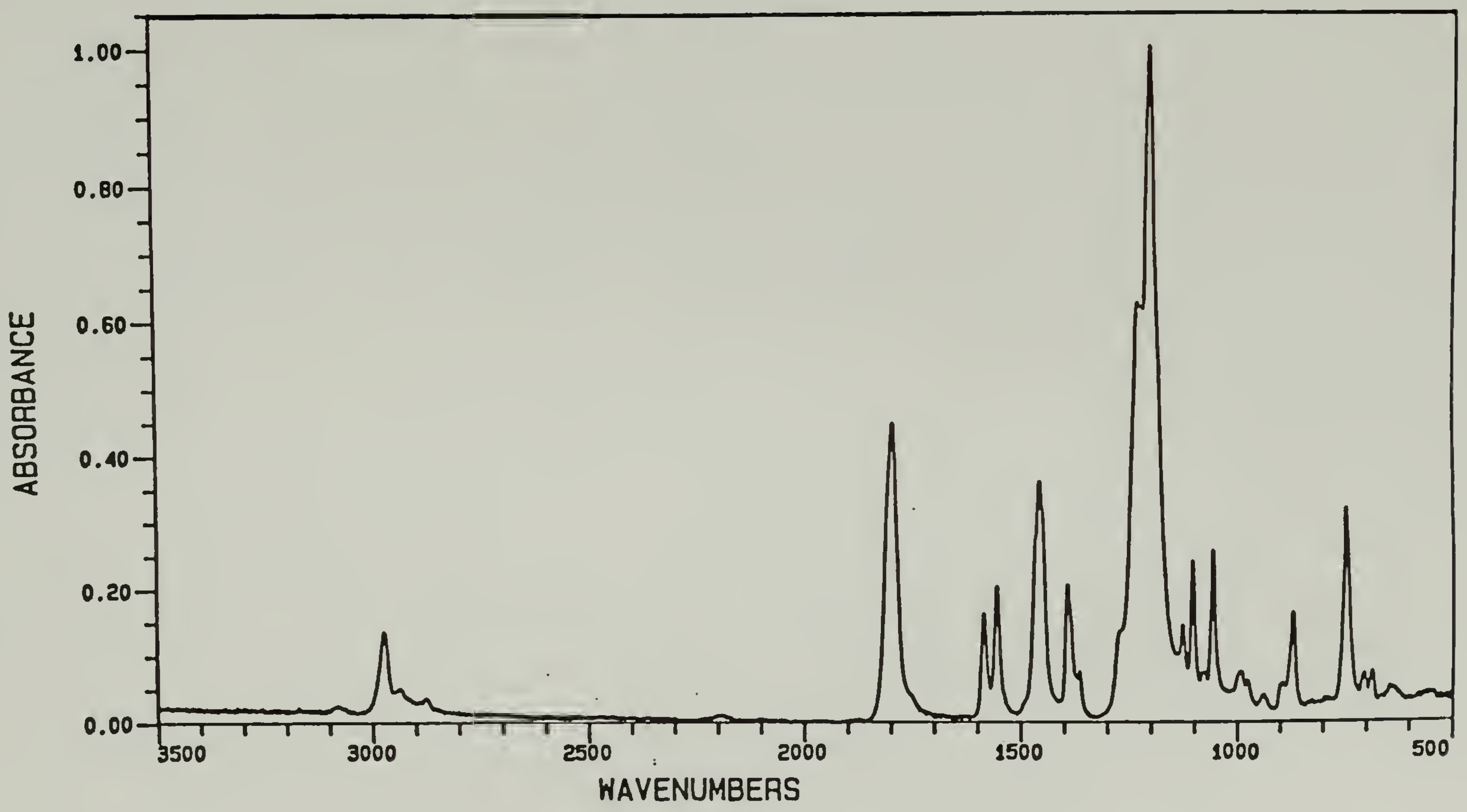

Figure A.5. FT-IR spectrum of tetrabromobisphenol-A polycarbonate (TBPC).

APPENDIX B

COMPUTER PROGRAM FOR FITTING MISCIBILITY WINDOW BOUNDARIES

```
' Program  CONICS    ellipses and hyperbolas
'
'
'Determines the coefficients of the equation
'   Ax^2 + Bxy + Cy^2 + Dx + Ey + F = 0
'
' The input s to the program are a, b, theta, h, and k,
'     a = major axis of ellipse, hyperbola
'     b = minor axis of ellipse, hyperbola
'     theta = angle of tilt of the ellipse, hyperbola
'     (h,k) = coordinates of lower part of ellipse with
       B = 0, or, for a hyperbola, the coordinates of the
       lowest point of the upper curve or the coordinates of
       the highest point if considering the lower curve (same
       logic for left and right hand side of horizontally
       oriented hyperbolas)
'
' Algorithm #2 is default for ellipse
'
'
axis$ = "HORIZONTAL"
DIM w(404), z(404)
CLS
CONST PI = 3.141592653589#
PRINT
PRINT
'
' SET THE BLEND SYSTEM MANUALLY BEFORE RUNNING THE PROGRAM
   --THIS WILL SET THE PROPER TEMPLATE
'
BLEND$ = "BTC"
PRINT TAB(21); "SELECTION OF ELLIPSE OR HYPERBOLA"
PRINT
PRINT TAB(30); "1)   ELLIPSE"
PRINT
PRINT TAB(30); "2)   HYPERBOLA"
INPUT ELLIPSE
PRINT CHR$(12)
SELECT CASE ELLIPSE
 CASE 2
  PRINT TAB(21); " SELECTION OF HYPERBOLIC CURVE"
  PRINT
  PRINT
  PRINT TAB(27); "1) VERTICAL, UPPER CURVE"
```

```
PRINT
PRINT TAB(27); "2) VERTICAL, LOWER CURVE"
PRINT
PRINT TAB(27); "3) HORIZONTAL, LEFT-HAND CURVE"
PRINT
PRINT TAB(27); "4) HORIZONTAL, RIGHT-HAND CURVE"
INPUT HYP
PRINT CHR$(12)
PRINT TAB(20); "WHAT ARE THE A AND B VALUES?"
INPUT AA, BB
PRINT TAB(20); "WHAT IS THETA?"
INPUT THETA
PRINT TAB(20); "WHAT IS (H,K) ?"
INPUT H, K
THETA = 2 * PI * THETA / 360
IF HYP = 1 OR HYP = 2 THEN
  a = -((1 / BB) ^ 2)
  b = 0
  c = (1 / AA) ^ 2
  d = 0
  IF HYP = 1 THEN e = (2 / AA) ELSE e = (-2 / AA)
ELSE
  a = (1 / AA) ^ 2
  b = 0
  c = -((1 / BB) ^ 2)
  IF HYP = 3 THEN d = (-2 / AA) ELSE d = (2 / AA)
  e = 0
END IF
ASTAR = (a * ((COS(THETA)) ^ 2)) + (c * ((SIN(THETA)) ^
         2))
BSTAR = (a - c) * SIN(2 * THETA)
CSTAR = (a * ((SIN(THETA)) ^ 2)) + (c * ((COS(THETA)) ^
         2))
IF HYP = 1 OR HYP = 2 THEN
 DPRIME = (-e) * SIN(THETA)
 EPRIME = e * COS(THETA)
ELSE
 DPRIME = d * COS(THETA)
 EPRIME = d * SIN(THETA)
END IF
DSTAR = DPRIME - (2 * ASTAR * H) - (BSTAR * K)
ESTAR = EPRIME - (2 * CSTAR * K) - (BSTAR * H)
FSTAR = (ASTAR * (H ^ 2)) + (BSTAR * H * K) + (CSTAR * (K
         ^ 2)) - (DPRIME * H) - (EPRIME * K)
a = ASTAR
```

```
  b = BSTAR
  c = CSTAR
  d = DSTAR
  e = ESTAR
  f = FSTAR
 CASE 1
  PRINT
  PRINT TAB(21); "SELECTION OF ELLIPTICAL ORIENTATION"
  PRINT
  PRINT
  PRINT TAB(9); "Please choose the axis along which the
                major axis is aligned"
  PRINT
  PRINT
  PRINT TAB(31); "1)  Horizontal"
  PRINT
  PRINT TAB(31); "2)  Vertical"
  INPUT jump
  IF jump = 2 THEN axis$ = "VERTICAL"
'
'  Now we know if ellipse is going to be vertically or
   horizontally referenced
'
  PRINT CHR$(12)
  INPUT "A and B values"; AA, BB
  INPUT "THETA value"; THETA
  INPUT "H and K values"; H, K
  IF axis$ = "VERTICAL" THEN
   xxx = AA
   AA = BB
   BB = xxx
  END IF
  PRINT CHR$(12)
'
' Set to calculate the coefficients
'
' First, THETA must be converted to radians
'
  THETA = 2 * PI * THETA / 360
'
'
'
  L = (COS(THETA) / AA) ^ 2
  m = (SIN(THETA) / BB) ^ 2
  theta2 = 2 * THETA
```

```
  aaa = 1 / (AA ^ 2)
  bbb = 1 / (BB ^ 2)
  o = (SIN(THETA) / AA) ^ 2
  n = (COS(THETA) / BB) ^ 2
  a = L + m
  b = (aaa - bbb) * SIN(theta2)
  c = n + o
'
' Time for algorithm selection  --  algo 2 is chosen
'
  algo = 2
  SELECT CASE algo
   CASE 1
    d = ((-2) * H * a) - (K * b)
    e = (-(H) * b) - (2 * K * c)
    f = (ASTAR * (H ^ 2)) + (b * H * K) + (c * (K ^ 2)) - 1
   CASE 2
    d = (2 * SIN(THETA) / BB) - (2 * a * H) - (b * K)
    e = ((-2) * COS(THETA) / BB) - (b * H) - (2 * c * K)
    f = (a * (H ^ 2)) + (b * H * K) + (c * (K ^ 2)) - (H * 2
        * SIN(THETA) / BB) - (K * (-2) * COS(THETA) / BB)
   END SELECT
 END SELECT

'  Now have A, B, C, D, E, and F.
'
'  Find the roots which fit on the miscibility map where
'      0 <= x <= 1 and 0<= y <=1
'
'  The roots are found using the quadratic equation.  For
   speed and space filling purposes, the formula is used
   along the x and y axes.  This fills in the gaps left when
   only on axis is used.
'
counter = 0
DIM root(2)
FOR x = 0 TO 1 STEP .01
'
'  Along the x-axis first
'
 zz = (a * (x ^ 2)) + (d * x) + f
 yy = (b * x) + e
 IF ((yy ^ 2) - (4 * c * zz)) >= 0 THEN
  root(1) = (-yy + SQR((yy ^ 2) - (4 * c * zz))) / (2 * c)
  root(2) = (-yy - SQR((yy ^ 2) - (4 * c * zz))) / (2 * c)
```

```
    FOR jj = 1 TO 2
     IF root(jj) <= 1 AND root(jj) >= 0 THEN
      counter = counter + 1
      w(counter) = x
      z(counter) = root(jj)
     END IF
    NEXT jj
   END IF
  NEXT x
 '
 '  Now the y-axis
 '
 FOR x = 0 TO 1 STEP .01
  zz = (c * (x ^ 2)) + (e * x) + f
  yy = (b * x) + d
  IF ((y ^ 2) - (4 * a * zz)) >= 0 THEN
   root(1) = (-yy + SQR((yy ^ 2) - (4 * a * zz))) / (2 * a)
   root(2) = (-yy - SQR((yy ^ 2) - (4 * a * zz))) / (2 * a)
   FOR jj = 1 TO 2
    IF root(jj) <= 1 AND root(jj) >= 0 THEN
     counter = counter + 1
     w(counter) = root(jj)
     z(counter) = x
    END IF
   NEXT jj
  END IF
NEXT x
'
'  Roots have been found; time to plot the data
'
'  Draw "box" and tick marks and fill-in with data
'
SCREEN 2
VIEW (0, 0)-(480, 199)
WINDOW (-.15, -.15)-(1.15, 1.15)
LINE (0, 0)-(1, 1), , B
'
' The "box" has just been drawn for the data
'
' Tick marks are needed now
'
FOR I = 1 TO 9
 LINE (I / 10, .01)-(I / 10, 0)
 LINE (I / 10, .99)-(I / 10, 1)
 LINE (.01, I / 10)-(0, I / 10)
```

```
 LINE (.99, I / 10)-(1, I / 10)
NEXT I
'
'  Let's plot the data on the graph
'
'  FIRST, LET'S PLOT THE MISCIBILITY DATA
'
SELECT CASE BLEND$
 CASE "BTC"
'   IMMISCIBLE DATA FIRST
FUN:  DATA
0,.06,.098,.133,.205,.243,.311,.417,.54,.668,.746,.776,999
  DATA 0,.06,.098,.133,.205,.243,.668,.746,.776,999
  DATA 0,.06,.098,.746,999
  DATA 999
  DATA .776,999
'   MISCIBLE
FUN2:  DATA 999
  DATA .311,.417,999
  DATA .133,.205,.243,.311,.417,.54,999
  DATA 0,.06,.098,.133,.205,.243,.311,.417,.54,.668,999
  DATA 0,.06,.098,.133,.205,.243,.311,.417,.54,.668,.746,999
  FOR ARG = 1 TO 2
   SELECT CASE ARG
    CASE 1
     '  PLOT IMMIS DATA
     RESTORE FUN
     FOR I = 0 TO 1 STEP .25
      x = 0
      DO UNTIL x = 999
      READ x
      CIRCLE (x, I), .006
      LOOP
     NEXT I
    CASE 2
     ' PLOT MISC DATA
     RESTORE FUN2
     FOR I = 0 TO 1 STEP .25
      x = 0
      DO UNTIL x = 999
      READ x
      CIRCLE (x, I), .006
      PAINT (x, I), 1
      LOOP
     NEXT I
```

```
   END SELECT
   NEXT ARG
   END SELECT

   FOR x = 1 TO counter
    PSET (w(x), z(x)), 1
   NEXT x
'
 Print quadratic equation coefficients
'
PRINT a, b, c, d, e, f
```

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