



*Institute of Paper Science and Technology
Atlanta, Georgia*

IPST Technical Paper Series Number 882

Synthesis and Characterization of Cationic Copolymers of Butyl Acrylate and
[3-(Methacryloylamino)propyl]trimethylammonium Chloride

Z. Yan, Y. Deng, D. Zhang, and C.Q. Yang

October 2000

Submitted to
Journal of Polymer Science
Polymer Chemistry Edition

Copyright® 2000 by the Institute of Paper Science and Technology

For Members Only

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is an independent graduate school, research organization, and information center for science and technology mainly concerned with manufacture and uses of pulp, paper, paperboard, and other forest products and byproducts. Established in 1929 as the Institute of Paper Chemistry, the Institute provides research and information services to the wood, fiber, and allied industries in a unique partnership between education and business. The Institute is supported by 50 member companies. The purpose of the Institute is fulfilled through four missions, which are:

- to provide a multidisciplinary graduate education to students who advance the science and technology of the industry and who rise into leadership positions within the industry;
- to conduct and foster research that creates knowledge to satisfy the technological needs of the industry;
- to provide the information, expertise, and interactive learning that enables customers to improve job knowledge and business performance;
- to aggressively seek out technological opportunities and facilitate the transfer and implementation of those technologies in collaboration with industry partners.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

The Institute of Paper Science and Technology assures equal opportunity to all qualified persons without regard to race, color, religion, sex, national origin, age, disability, marital status, or Vietnam era veterans status in the admission to, participation in, treatment of, or employment in the programs and activities which the Institute operates.

Synthesis and Characterization of Cationic Copolymers of Butyl Acrylate and [3-(Methacryloylamino)propyl]trimethylammonium Chloride

Zegui Yan and Yulin Deng *

Institute of Paper Science and Technology, Atlanta, GA 30318, USA

Dong Zhang and Charles Q. Yang

Department of Textiles, University of Georgia, GA 30602, USA

Abstract

Cationic copolymers of butyl acrylate (BA) and [3-(methacryloylamino)propyl]-trimethylammonium chloride (MAPTAC) were synthesized by free radical solution polymerization in methanol or ethanol. FT-Raman and nuclear magnetic resonance (NMR) were applied to monitor the polymerization process. The copolymers were characterized by light scattering, NMR, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). It was found that random copolymers could be prepared, and the molar fractions of butyl acrylate and cationic monomers in the copolymers were close to the feed ratios. The copolymer prepared in methanol has higher molecular weight than that prepared in ethanol. With increased cationic monomer content, the glass transition temperature (T_g) of the copolymer increases, while the thermal stability decreases. The reactivity ratios for the monomers were evaluated. Copolymerization of BA (M_1) with MAPTAC (M_2) gave reactivity ratios as $r_1=0.92$ and $r_2=2.61$ in ethanol, and $r_1=0.79$ and $r_2=0.90$ in methanol. This study indicated that a random copolymer containing a hydrophobic monomer, such as BA, and a cationic

* Author to whom correspondence should be addressed.

hydrophobic monomer, such as MAPTAC, can be prepared by choosing a correct polar solvent, such as methanol or ethanol.

[ZY1]

Introduction

Synthesis of copolymers containing both hydrophobic and cationic hydrophilic units has been studied intensively. Emulsion polymerization techniques have been applied to synthesize cationic polymeric latexes, which have shown potential applications as catalysts [1, 2], papermaking aids [3-6], and coating agents [7]. However, there are several problems in using emulsion polymerization techniques for preparation of this type of copolymer. First, because cationic monomers are strongly hydrophilic and are not miscible with the hydrophobic monomers in water, the incorporation rate of cationic monomers to the polymer through direct emulsion polymerization has been low. Brouwer [8] studied the emulsion polymerization of styrene (80-100 wt%) and [2-(methacryloxy)ethyl]trimethylammonium chloride (MAETAC, 0-20 wt%), and found that the maximum incorporation of MAETAC to the latex was less than 4 wt%. Second, because the solubility of cationic monomers in water is significantly different from that of hydrophobic monomers, the emulsion copolymerization of these two different monomers usually results in two polymeric fractions, i.e., a high-cationic-monomer-containing copolymer and a high-hydrophobic-monomer-containing copolymer [9]. Third, emulsion polymerization cannot be used to prepare a high-cationic-containing copolymer because the copolymer will be water soluble and it cannot exist in a latex form in water if the cationic content is high.

Copolymers containing both hydrophobic and cationic hydrophilic units with a high cationic content have been synthesized by cationization of the copolymer that contained a functional monomer [2, 10-13]. The copolymerization of the hydrophobic monomer and cationic monomer in an organic solvent has also been used to synthesize these types of copolymers [12-15]. These copolymers have potential application as adhesive curing agents [12], controlled drug release agents [14], and ion-exchange membranes [15]. Although copolymers with a high cationic content have already been made for various applications, the synthesis of these types of copolymers by solution polymerization has not been well addressed. In this study, a series of poly(BA-co-MAPTAC) copolymers with different cationic content was synthesized by solution polymerization and characterized. The effect of reaction conditions on the properties of the copolymers was studied, and the reaction kinetics was reported.

When solution polymerization is used to prepare a homogeneous poly(BA-co-MAPTAC), the choice of the right solvent is critical. First, both BA (hydrophobic) and MAPTAC (cationic and hydrophilic) should be soluble in the solvent used. Second, the solvent should also be a good solvent for the copolymer to prevent the precipitation of the copolymers. Third, both monomers should have reasonable monomer reactivity ratios in the solvent. Because both ethanol and methanol are strong polar organic solvents, it is expected that they can fit these requirements.

Experimental

Materials

All chemicals were purchased from Aldrich Chemical Company. Butyl acrylate (BA, 99+%) and ethylene glycol dimethylacrylate (EGMA) were washed with 5% sodium hydroxide aqueous solution three times and then with deionized water three times to remove inhibitors. [3-(Methacryloylamino)propyl]trimethylammonium chloride (MAPTAC, 50 wt% in water) was extracted with ethyl ether five times to remove inhibitors, and the residual ethyl ether was removed by a rotary evaporator at room temperature under reduced pressure. 2,2'-Azobisisobutyronitrile (AIBN), methanol, and ethanol were used as received. Solvents used were all HPLC grades.

Copolymer Synthesis

Copolymers were synthesized by solution polymerization in methanol or ethanol. A typical example (Sample P3 in Table 1) is as follows: a 250ml three-neck round flask equipped with a thermometer, nitrogen inlet, condenser, and mechanical stirrer was charged with 25.6 g of BA (0.20 mol), 7.8 g of MAPTAC (0.035 mol), 42.9 g of ethanol. The mixture was purged with nitrogen for 30 minutes and heated to 65°C. After temperature reached equilibrium, 0.193 g of AIBN (1.18 mmol) in about 5 ml ethanol was injected. The mixture was kept at 65°C for 4 hours. After cool down, the mixture was poured into a large amount (~250 ml) of hexane with stirring, and then the bottom layer was washed repeatedly with hexane (3x100 ml). The purified polymer was dried first in air and then at 40°C for 24 hrs under vacuum.

Characterization

Raman spectra were recorded on a Nicolet 950 FT-Raman Spectrometer with an InGaAs detector to monitor the polymerization process. The resolution was 8 cm^{-1} and there were 200 scans for each spectrum. $^1\text{H-NMR}$ spectra were recorded on a Mercury 300MHz NMR spectrometer in deuterium solvents to determine the composition of the polymer or to quantitatively monitor the monomer contents during the polymerization process. Glass transition temperatures were determined on a Perkin Elmer Pyris-1 differential scanning calorimeter under helium atmosphere. All the samples were first heated to 150°C , then cooled to -70°C and reheated to 150°C at the rate of $40^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA851 instrument. All the samples were heated from 25°C to 500°C at the rate of $20^\circ\text{C}/\text{min}$ in air atmosphere.

The refractive index increment, dn/dc , of the copolymers was measured on a Waters 410 Differential Refractometer, which was calibrated by using NaCl aqueous solutions. The molecular weight of the polymer was determined on a GPC-MALLS light scattering system with a Waters GLC/GPC 244 apparatus in combination with a Dawn DSP MALLS light scattering photometer (Wyatt Technology Co.). Dimethylformamide (DMF) with a flow rate of $0.8\text{ ml}/\text{min}$ was used as mobile phase at room temperature.

Results and Discussion

Polymerization

Copolymers synthesized from solution polymerization are listed in Table 1. The polymerization process could be monitored by Raman spectroscopy. Figure 1 shows the

Raman spectra collected in the polymerization process of synthesizing copolymer P10. Figure 1A was the spectrum of the reaction mixture at the beginning of the polymerization. The bands at 3108 and 3040 cm^{-1} are the stretching modes of unsaturated =C-H of the monomers. The strong band at 1638 cm^{-1} and the band at 1412 cm^{-1} are due to the stretching mode and in-plane bending of the alkene C=C of the monomers, respectively. The band at 1714 cm^{-1} is the carboxylate carbonyl stretching mode. The wide bands at 2942, 2877, 2835, 1453, and 1299 cm^{-1} are the symmetric or asymmetric stretching or bending modes of CH_3 or CH_2 of the monomers and methanol. When the polymerization mixture was kept at 65°C for 30 min, all the bands of the alkene C=C at 3108, 3040, 1638, and 1413 cm^{-1} have diminished as shown in Figure 1B. After the polymerization was kept for four hours, all the bands of the alkene C=C disappeared (see Figure 1C). During the polymerization process, the frequency of the carbonyl band shifted from 1714 cm^{-1} (monomers) to 1728 cm^{-1} (polymers). When monomers polymerized to form polymers, the unsaturated C=C bonds of monomers were converted to saturated C-C bonds, and the carboxylate carbonyl was no longer conjugated with C=C, thus the band shift to a higher frequency. With the aid of the FT-Raman spectrum, the progress of the polymerization can be conveniently monitored. However, it was also found that the sensitivity of FT-Raman is not high enough to quantitatively monitor the polymerization process. It was also difficult to distinguish the BA and MAPTAC with FT-Raman. Therefore, the copolymerization kinetics of this reaction was studied using NMR, as described later.

Molecular Weight

The molecular weights of the copolymers were determined with a GPC-MALLS light scattering system and are listed in Table 1. Comparing the molecular weights of copolymers synthesized in different solvents, it is obvious that the molecular weights of the copolymers synthesized in methanol were much higher than those synthesized in ethanol. The reason may be that the chain transfer constant of methanol ($C_s=1.4 \times 10^{-2}$ at 60°C) is smaller than that of ethanol ($C_s=2.8 \times 10^{-2}$ at 60°C) [16]. Introducing a small amount of crosslinker EGDM significantly increased the molecular weight of the copolymer, but gelation occurred when crosslinker content was higher than 0.4%.

Compositions

The composition of the resulting copolymer was determined from $^1\text{H-NMR}$. A typical $^1\text{H-NMR}$ spectrum of BA/MAPTAC copolymer in CDCl_3 is shown in Figure 2. Chemical shifts of 4.0 ppm and 3.40 ppm were assigned to the OCH_2 of BA and $\text{N}^+(\text{CH}_3)$ of MAPTAC, respectively. The composition of the copolymer was calculated from the integration ratio of the two peaks. The feed ratios of various monomer mixtures, as well as the composition of the resulting copolymers, were summarized in Table 1. It can be seen that the molar fractions of butyl acrylate and cationic comonomer in the copolymer were all close to the feed ratios.

The GPC chromatogram indicated that there was only one major peak for every copolymer. In an emulsion copolymerization of styrene and MAPTAC, van Streun and his coworkers [9] found that two fractions of copolymers (a high MAPTAC containing and a high styrene containing fractions) were formed when the cationic monomer feeding

ratio is high. They indicated that the formation of two fractions was due to the significant difference in the solubility of two monomers. However, because the solvents used in this study are good solvents for both monomers of BA and MAPTAC and the copolymers, homogeneous copolymers are expected. The single peak of GPC supports that no homopolymers were presented in these systems. In order to further verify that the resulting polymers were uniform copolymers, some polymers were dissolved in chloroform and extracted with water. The compositions of the two fractions in water (a good solvent for polyMAPTAC) and chloroform (a good solvent for polybutyl acrylate) were measured by $^1\text{H-NMR}$, and no apparent composition difference was found from the copolymers obtained from these two fractions. Therefore, it was concluded that the resulting copolymers are homogeneous copolymers.

Copolymerizability

The polymerization process was monitored quantitatively by NMR in CD_3OD , in which both the monomers and the resulting polymers were soluble. Figure 3a shows the NMR spectrum of a BA and MAPTAC mixture in methanol before initiator was added. Figure 3b shows the NMR spectrum of the above mixture after 10 minutes of polymerization. Conversion of BA was determined by change of the signal integration ratio of OCH_2 protons (from δ 4.16 ppm for monomer to 4.08 ppm for polymer), and conversion of MAPTAC was determined by change of the signal integration ratio of $\text{N}^+(\text{CH}_3)_3$ protons (from δ 3.14 ppm for monomer to 3.22 ppm for polymer). The copolymer composition was calculated from the signal integration ratio of OCH_2 protons and $\text{N}^+(\text{CH}_3)_3$ protons in polymer.

Figure 4 shows the time-conversion curves for the copolymerization of BA with MAPTAC in ethanol (Sample P3). It shows that the reactivity rate of MAPTAC is much higher than that of BA. To further understand the copolymerizability of BA and MAPTAC, their reactivity ratios were measured. Monomer reactivity ratios were evaluated by the graphical method according to the Fineman and Ross equation [17]:

$$\frac{F(f-1)}{f} = r_1 \frac{F^2}{f} - r_2 \quad (1)$$

where r_1 and r_2 are the reactivity ratios relating to BA (M_1) and MAPTAC (M_2), respectively; $F = d[M_1]/d[M_2]$ is the ratio of the numbers of each kind of repeat unit in the polymer; and $f = [M_1]/[M_2]$ is the monomer molar feed ratio. Monomer reactivity ratios were also obtained by using the Kelen-Tudos method [18], which is a refined linearization method from the Fineman and Ross method.

Details of the copolymerization of BA with MAPTAC in ethanol and methanol are listed in Tables 2 and 3, respectively. The monomer reactivity ratios calculated from both the Fineman-Ross method and the Kelen-Tudos method are shown in Table 4. It is interesting to note that the solvents (ethanol and methanol) did not have a big effect on the relative copolymerizability of BA, but had a significant effect on that of MAPTAC. The high MAPTAC reactivity ratio in ethanol may be due to a "microphase separation effect" [19]. It is known that MAPTAC is more soluble in methanol than in ethanol [20]. The tendency for MAPTAC monomers to form aggregates in ethanol would be higher, and thus it would be more favorable for MAPTAC to have homopolymerization in ethanol than in methanol. To further understand the blockiness of the copolymer, the statistical distribution of monomer sequences M_1 - M_1 , M_2 - M_2 , and M_1 - M_2 in the BA/MAPTAC copolymers was calculated by the method of Igarashi [21]. Table 5 lists

the structural data for the copolymers. The calculated mol% of M_1 - M_2 linkages is much higher than that of M_2 - M_2 linkages for all the copolymers, indicating that the blockiness of the MAPTAC is low even for copolymers prepared in ethanol. The low blockiness of MAPTAC is further indicated by the low mean sequence length value for MAPTAC in the copolymer. The reasons for this are the low MAPTAC feed ratio in the copolymerization and BA's preference for copolymerization. The results indicate that the difference of the monomer sequence distribution for the copolymers prepared in ethanol and methanol with a low MAPTAC content is not significant.

Thermal analysis

The glass transition temperatures (T_g) of the PSA samples were determined by DSC, and the results are shown in Figure 5. It is obvious that with increased cationic content, the T_g of the copolymer increases. Copolymers synthesized in methanol showed slightly higher T_g , which may be due to the higher molecular weight of the copolymer. Generally, copolymers from different solvents with similar cationic content showed very similar T_g .

Thermogravimetric analyses (TGA) of the copolymers were also conducted. Figure 6 shows the TGA curves of copolymers P1-P4. It clearly indicates that all copolymers begin to decompose at 230°C with three stages of weight loss. With increased cationic MAPTAC content, the first stage of weight loss increases correspondingly. This stage of weight loss may be attributed to the thermal instability of the MAPTAC units in the copolymer. Copolymers synthesized in methanol showed similar TGA curves. Figure 7 shows the temperature at 10% weight loss of the copolymer as a function of the

MAPTAC content in the copolymer. No obvious difference of thermal stability was found for copolymers with the same MAPTAC content but synthesized in different solvents.

Conclusion

Homogeneous copolymers of hydrophobic BA and hydrophilic cationic MAPTAC can be synthesized by solution copolymerization in ethanol or methanol. The polymerization process was monitored by FT-Raman and NMR. The molecular weights of the copolymers were measured by GPC and light scattering. It was found that the copolymer prepared in methanol has much higher molecular weight than that prepared in ethanol, and the molecular weight of the copolymer could also be effectively increased by incorporating a small amount of crosslinker.

Copolymerization of BA with MAPTAC in ethanol and methanol yields very different values of reactivity ratio for MAPTAC. The high reactivity ratio of MAPTAC in ethanol may be due to the microphase separation effect.

Thermal analyses of the copolymers indicate that with increased cationic monomer content, the T_g of the copolymer increases, and the thermal stability decreases. Thermal analysis results further showed that copolymers from different solvents with the same MAPTAC content had very similar glass transition temperatures (T_g) and thermal stability.

Acknowledgement

The authors thank the U.S. Department of Energy (DOE) for their financial aid.

References

1. Bernard, M.; Ford, W. T.; Taylor, T. W. *Macromolecules* **1984**, 17, 1812.
2. Ford, W. T.; Yu, H. *Langmuir* **1999**, 9, 1999.
3. Alice, B. *Tappi J.* **1977**, 60, 133.
4. Inoue, M.; Alice, B.; Shao, Y.; Van de Ven, T. *Proceedings of 1996 International Paper and Coating Chemistry Symposium, CPPA*, **1996**, 199.
5. Ono, H.; Deng, Y. *J. Colloid Interface Sci.* **1997**, 188, 183.
6. Ono, H.; Deng, Y. *Proceedings of 1997 TAPPI Engineering and Papermakers Conference*, TAPPI Press, **1997**, 837.
7. Ishikawa, O.; Sasagawa, Y.; Tsuji, A.; Yamashita, T. *Jpn Tappi J.* **1993**, 47, 334.
8. Brouwer, W. M.; van Haeren, M.; van Haeren, P.; *Eur. Polym. J.* **1990**, 26(1), 35.
9. Streun, K.; Belt, K.; Piet, P.; German, L.; *Eur. Polym. J.* **1990**, 27(2), 931.
10. Upson, D. *J. Polym. Sci. Polym. Symp.* **1985**, 72, 45.
11. Bon, S.; Beek, H.; Piet, P.; German, A. *J. Appl. Polym. Sci.* **1995**, 58, 19.
12. Otaigbe, J.; Banks R.; Smith, S. *Br. Polym. J.* **1988**, 20, 53.
13. Deng, Y.; Yan, Z.; Yang, N. *Colloid Polym. Sci.* **1999**, 277, 227.
14. Konar, N.; Kim, C. J. *J. Appl. Polym. Sci.* **1998**, 69, 263.
15. Nonaka, T.; Fujita, K. *J. Membr Sci.* **1998**, 144 (1-2), 187.
16. Ueda, A.; Nagai, S. in *Polymer Handbook*, 4th edition, Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds., J. Wiley & Sons, New York, **1999**, II-120.
17. Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, 5, 259.
18. Kelen, T.; Tudos, F. *J. Macromol. Sci. Chem.* **1975**, 9, 1.
19. Ledwith, A.; Galli, G.; Chiellini, E.; Solaro, R. *Polym. Bull.* **1979**, 1, 491.

20. Lee, W.-F.; Tsai, C.-C. *Polymer* **1994**, 35, 2210.

21. Igarashi, S. *J. Polym. Sci. Polym. Lett.* **1963**, 1, 359

Table 1. Characteristics of Copolymers

Sample	Solvent	EGDM (mol%)	Cationic unit fraction (mol%)		dn/dc	$M_w/10^5$ (g/mol)
			in feed	in polymer		
P1	ethanol	0	5.0	5.7	0.045	2.3
P2	ethanol	0	10.0	10.6	0.051	1.8
P3	ethanol	0	15.0	15.2	0.063	1.4
P4	ethanol	0	20.0	20.9	0.066	2.3
P5	ethanol	0.2	15.0	17.6	0.063	8.6
P6	ethanol	0.5	15.0	17.3	0.063	13
P7	ethanol	0.8	15.0	-	-	*
P8	methanol	0	5.0	5.7	0.045	6.3
P9	methanol	0	10.0	10.8	0.051	7.8
P10	methanol	0	15.0	16.2	0.063	8.3
P11	methanol	0	20.0	21.9	0.066	9.7
P12	methanol	0.1	15.0	17.4	0.057	19
P13	methanol	0.2	15.0	-	-	*

* Gel was formed during copolymerization.

Table 2. Copolymerization of BA (M_1) with MAPTAC (M_2) in Ethanol

$f = \frac{[M_1]}{[M_2]}$	Time (min)	Conversion (%)		$F = \frac{d[M_1]}{d[M_2]}$
		M_1	M_2	
7.71	4	9.8	12.7	5.96
4.87	4	9.2	12.2	3.69
3.52	5	8.1	11.7	2.44
2.53	5	7.0	11.2	1.59
1.52	5	5.2	8.9	0.89

Table 3. Copolymerization of BA (M_1) with MAPTAC (M_2) in Methanol

$f = \frac{[M_1]}{[M_2]}$	Time (min)	Conversion (%)		$F = \frac{d[M_1]}{d[M_2]}$
		M_1	M_2	
7.44	4	9.1	11.9	6.13
4.68	4	7.8	9.3	3.92
3.58	5	7.9	9.2	3.08
2.52	5	7.0	8.3	2.13
1.52	5	5.2	5.7	1.39

Table 4. Monomer reactivity ratios.

M_1	M_2	Solvent	Fineman-Ross Method		Kelen-Tudos Method	
			r_1	r_2	r_1	r_2
BA	MAPTAC	Ethanol	0.91	2.56	0.92	2.61
BA	MAPTAC	Methanol	0.79	0.93	0.79	0.90

Table 5. Structural data for the copolymers of BA (M_1) with MAPTAC (M_2)

Copolymer	M_1 in copolymer (mol%)	Blockiness (mol%)		Alteration (mol%)	Mean seq. length	
		M_1 - M_1	M_2 - M_2	M_1 - M_2	M_1	M_2
P1	94.3	89.3	0.70	0.10	18.9	1.14
P2	89.4	81.0	2.18	16.8	10.6	1.26
P3	84.8	73.7	4.23	22.1	7.66	1.37
P4	79.1	65.4	7.17	27.4	5.76	1.52
P8	94.3	88.8	2.34	10.9	17.3	1.04
P9	89.2	79.3	8.82	19.8	8.99	1.09
P10	83.8	69.6	2.05	28.3	5.92	1.14
P11	78.1	60.1	3.86	36.1	4.33	1.21

FIGURE CAPTIONS

Figure 1. FT-Raman of the reaction mixtures at different times in the synthesis of BA/MAPTAC copolymer (P10): (a) 0 minute; (b) 30 minutes; (c) 4 hours.

Figure 2. $^1\text{H-NMR}$ spectrum of BA/MAPTAC copolymer (P3) in CDCl_3 .

Figure 3. Typical $^1\text{H-NMR}$ spectra (in CD_3OD) of the reaction mixtures at different times in the synthesis of BA/MAPTAC copolymer in methanol: (a) 0 minute; (b) 10 minutes.

Figure 4. Time-conversion curves for the copolymerization of BA with MAPTAC in ethanol (P3).

Figure 5. Glass transition temperature (T_g) of BA/MAPTAC copolymers as a function of the MAPTAC content in the copolymer.

Figure 6. Thermogravimetric analysis (TGA) of BA/MAPTAC copolymers.

Figure 7. Thermogravimetric analysis of BA/MAPTAC copolymers: Temperature at 10% weight loss as a function of the MAPTAC content in the copolymer.

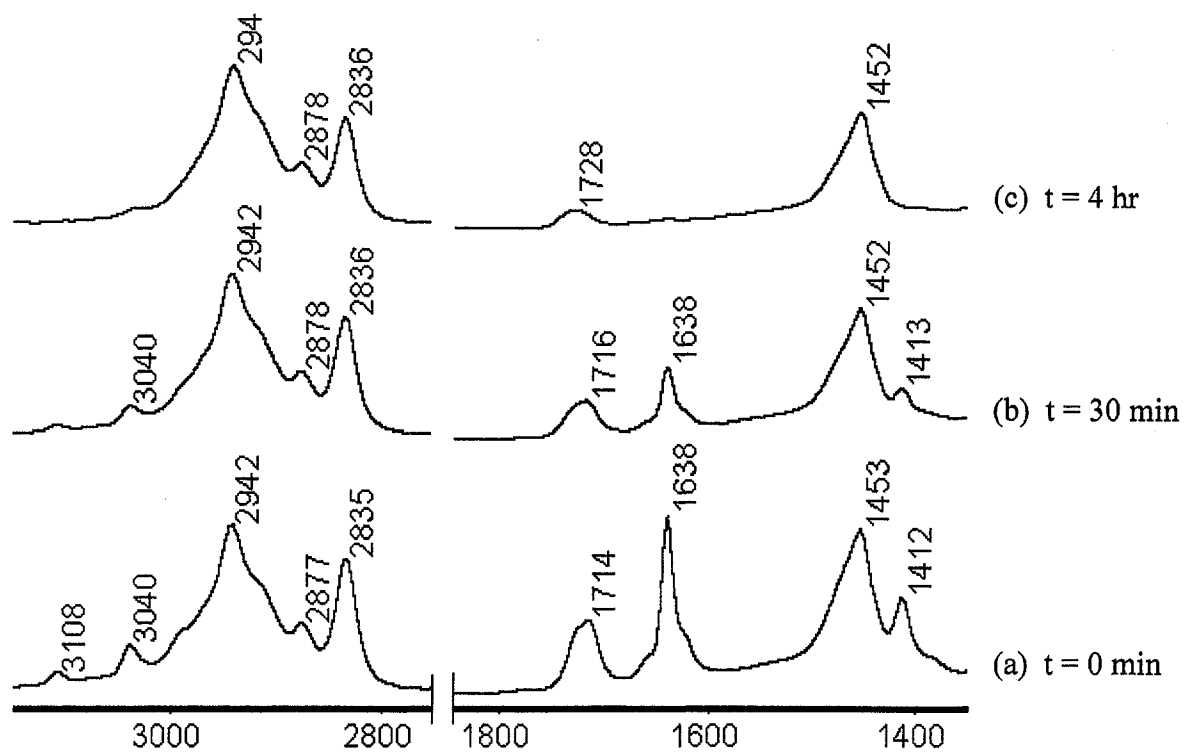


Figure 1. FT-Raman of the reaction mixtures at different times in the synthesis of BA/MAPTAC copolymer (P10): (a) 0 minute; (b) 30 minutes; (c) 4 hours.

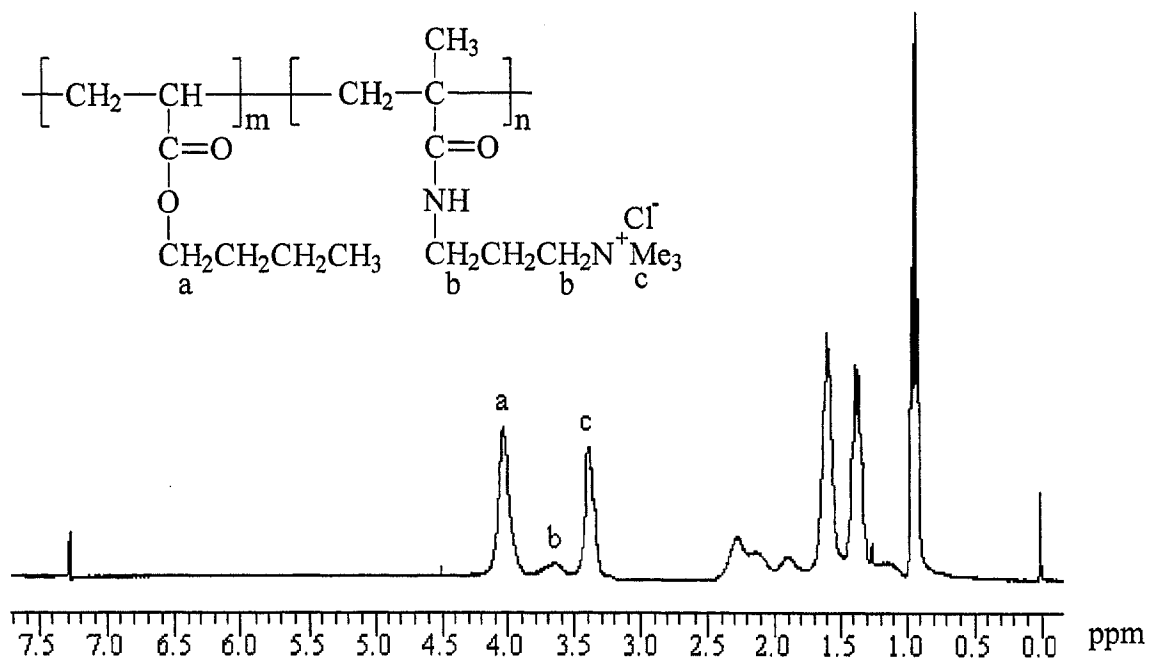


Figure 2. $^1\text{H-NMR}$ spectrum of BA/MAPTAC copolymer (P3) in CDCl_3 .

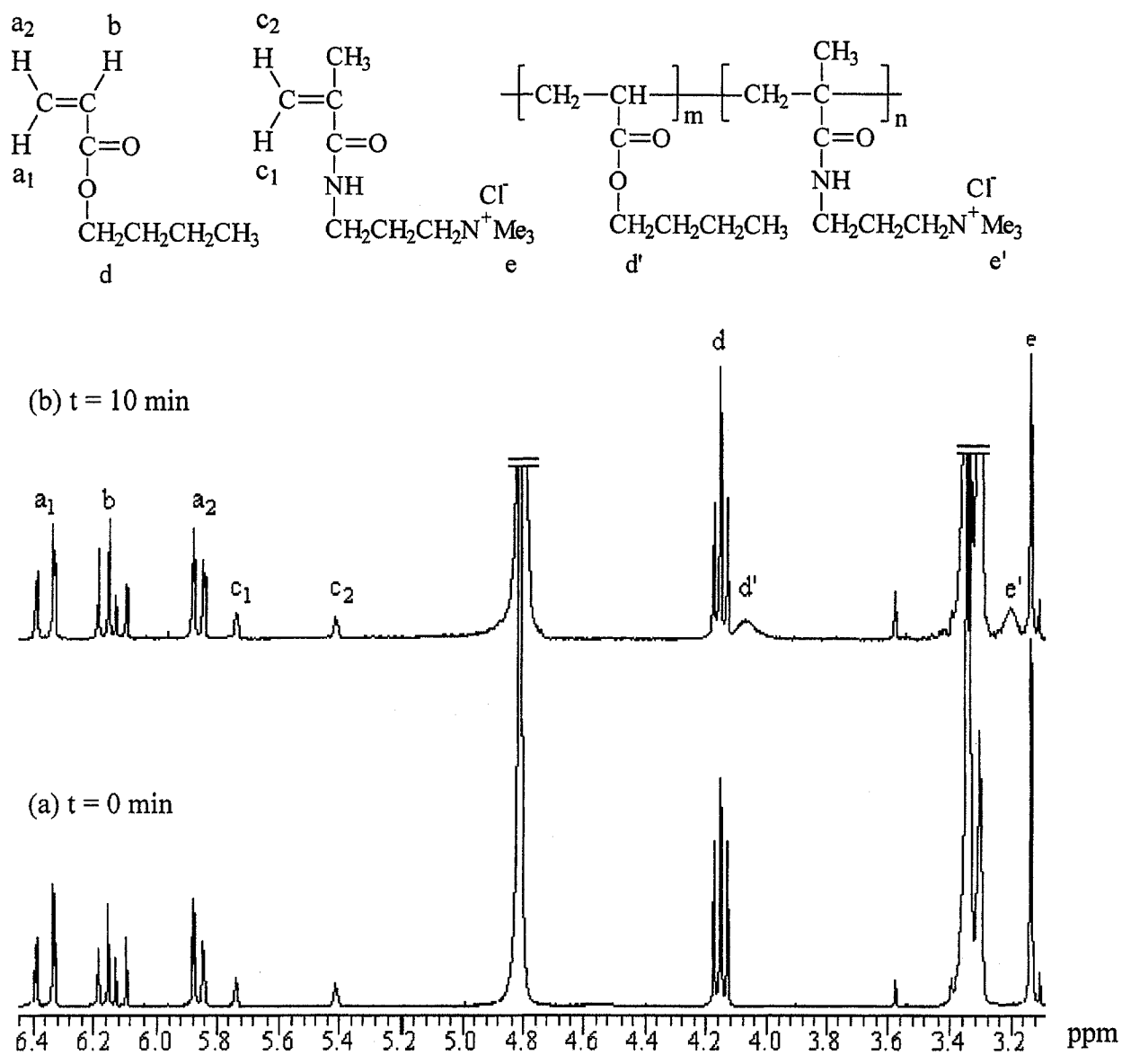


Figure 3. Typical ¹H-NMR spectra (in CD₃OD) of the reaction mixtures at different times in the synthesis of BA/MAPTAC copolymer in methanol: (a) 0 minute; (b) 10 minutes.

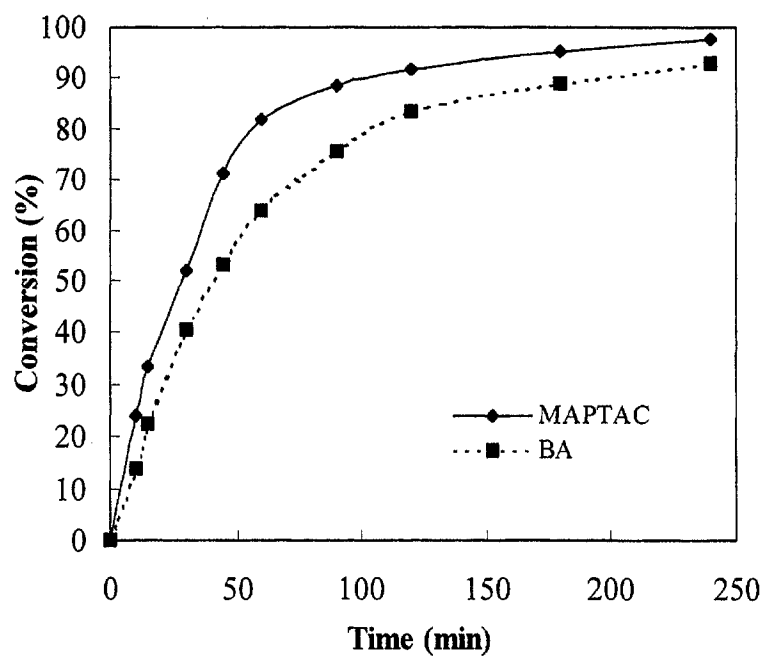


Figure 4. Time-conversion curves for the copolymerization of BA with MAPTAC in ethanol (P3).

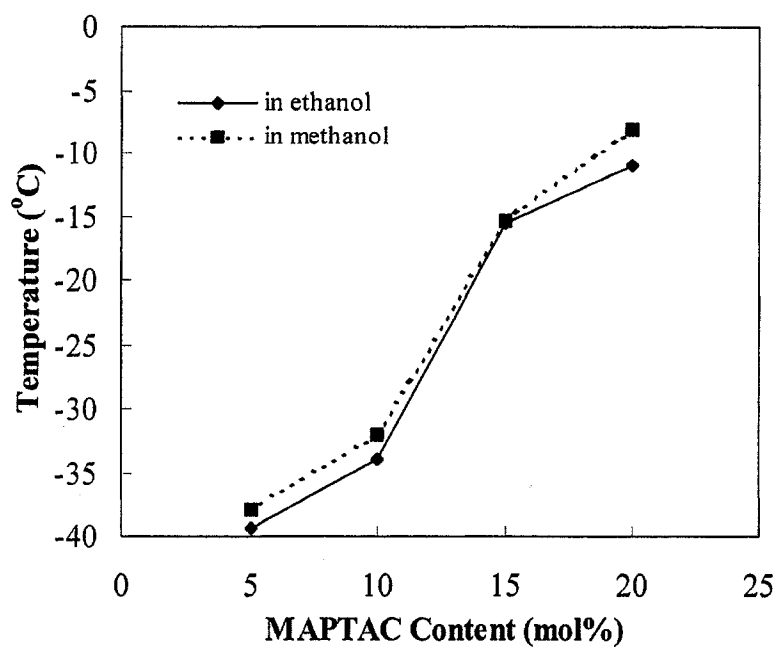


Figure 5. Glass transition temperature (T_g) of BA/MAPTAC copolymers as a function of the MAPTAC content in the copolymer.

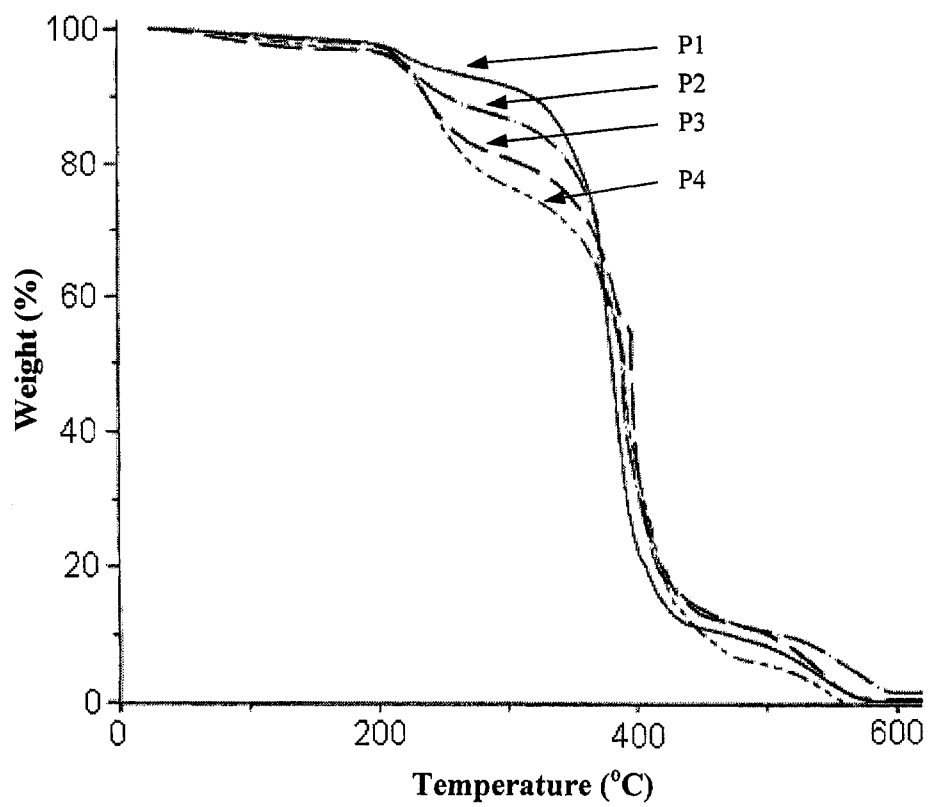


Figure 6. Thermogravimetric analysis (TGA) of BA/MAPTAC copolymers.

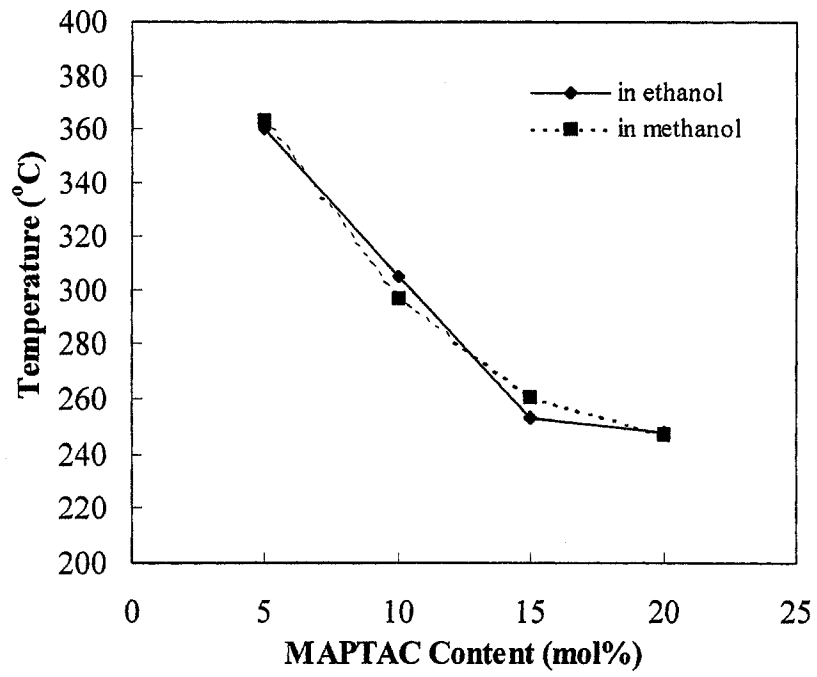


Figure 7. Thermogravimetric analysis of BA/MAPTAC copolymers: Temperature at 10% weight loss as a function of the MAPTAC content in the copolymer.

