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Macroporous Polymer Synthesis and Characterization: The Role of Molecular Recognition in the Regioselectivity of Sucrose Reactions

Gilbert Joshua Matare

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MACROPOROUS POLYMER SYNTHESIS AND CHARACTERIZATION

THE ROLE OF MOLECULAR RECOGNITION IN THE REGIOSELECTIVITY OF SUCROSE REACTIONS

By: Gilbert J. Matare

Date Submitted: 7/20/94

Approved by the Thesis Committee:

7-25-94
Date

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Date

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Date

MACROPOROUS POLYMER SYNTHESIS AND CHARACTERIZATION: THE ROLE OF MOLECULAR RECOGNITION IN THE REGIOSELECTIVITY OF SUCROSE REACTIONS

(TITLE)

BY

GILBERT JOSHUA MATARE

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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CHARLESTON, ILLINOIS

1994
YEAR

I HEREBY RECOMMEND THIS THESIS BE ACCEPTED AS FULFILLING
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ABSTRACT

MACROPOROUS POLYMER SYNTHESIS AND CHARACTERIZATION

THE ROLE OF MOLECULAR RECOGNITION IN THE REGIOSELECTIVITY OF SUCROSE REACTIONS

GILBERT J. MATARE

Molecular recognition has recently emerged as a unique technique for making synthetic polymers with selective binding cavities which can stereoselectively and regioselectively bind to a template molecule in a fashion similar to natural enzymes and antibodies. Its industrial applications in chemistry and biomedicine have been recently exploited. Typical examples include the resolution of amino acids, enantio-separation of racemates and bioactive molecules, selective binding of metal ions and in HPLC investigations. Our research is focused on applying molecular recognition studies to improve the regioselectivity of sucrose reactions.

Sucrose is an abundant industrial raw material of immense industrial importance however, its full commercial utilization is severely limited by the lack of regioselectivity

in many synthetic reactions. This is due to the eight reactive hydroxyl groups on the sucrose molecule. Our strategy is to use a molecule of similar structure to sucrose, in our case, p-nitrophenyl α-D-glucopyranoside, to serve as a template. From this, a monomer, p-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside is synthesized and copolymerized with styrene and divinylbenzene to form a three dimensional cross-linked polymer matrix. Removal of the template molecule from the polymer matrix by hydrolysis would create cavities on the polymer whose functional groups can "recognize" and bond to the template molecule and ultimately with the glucose end of sucrose. This way we can block the hydroxyls on the glucose part of sucrose from further reactions whilst a number of reactions can be done with the fructose hydroxyls. Alternatively a reaction might possibly be performed on the sucrose in the cavity.

Not much attention has been given to the set of experimental conditions necessary for the synthesis of polymer imprints which are macroporous, spherical and have a high surface area. In order for the polymers to be selective a macroporous state is very desirable since it permits access to a large surface area and thus a larger number of cavities. This thesis deals with the task of finding the necessary conditions for the synthesis of macroporous polymers, their characterization and surface area measurement.

DEDICATION

Dedicated to my precious sons Nathaniel and Benjamin.

ACKNOWLEDGEMENTS

My sincerest gratitude and thanks to Dr. Jerry W. Ellis for his professional assistance and guidance during the entire project. I wish to thank my wife for her encouragement and moral support.

Special thanks to all the faculty and staff of the Chemistry Department, especially Ken and Matt who always had just what I wanted.

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CHAPTER 1

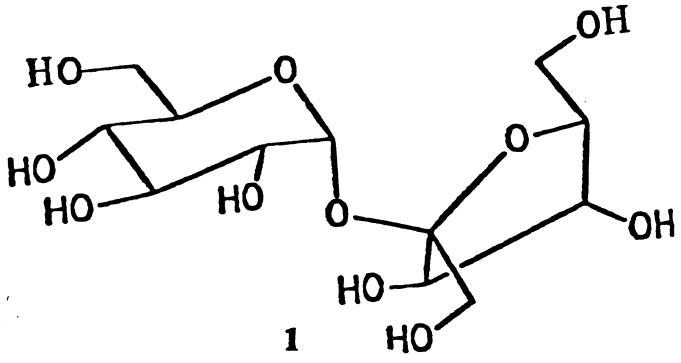
A. PROBLEMS OF REGIOSELECTIVITY IN SUCROSE REACTIONS

As the price of crude oil continues to climb,[1] more products from agriculture will be required as raw materials for the chemical industry. At present, crop surpluses in many countries have been largely wiped out by an increase in world population. The approaching depletion of our petroleum resources and the realization that even coal, oil shale and tar sands are not infinite in amount, have emphasized the importance of the utilization of renewable resources such as forest products and annual crops.

Thus, the long range view of industrial organic chemistry must inevitably foresee a continually decreased dependence upon fossil fuels. It is therefore reasonable to believe that sucrose **(1)** must inevitably be part of the wave of tomorrow to fill the gap left by the shortage of crude oil. Presently, no one knows exactly how much of that wave will be sucrochemical in nature, but the uniquely high productivity of sugar cane and sugar beet suggests that they will serve as very important sources of fuel and chemicals.[1]

Sucrose is an abundant resource of nearly matchless, molecular homogeneity, available at reasonable prices. Yet the prophet of utilization who has dared to roll up his/her sleeves and attempt sugar reactions in his/her laboratory, more often than not has

met stark frustration. Since the sucrose molecule contains three primary and five secondary hydroxyl groups, these are the logical points of attack. The small differences in the reactivities among the several hydroxyl groups in sucrose, in most reactions, have produced intractable and almost unresolvable mixtures of positional isomers with ranges of degrees of substitution.



1

The main focus of sucrochemistry has concentrated upon stereoselective chemical reactions by replacement of specific hydroxyl groups by other functional groups.[1] The progress that has been made in this field, despite the complexities associated with this molecule, has been due to the application of mass spectrometry, ^{1}H NMR and ^{13}C NMR to the structure determination of the products isolated by column chromatography. Sucrose and its derivatives show regioselectivity in many of their reactions, which is fortunate, since a large number of partially substituted derivatives are theoretically possible. This is shown in Table 1.

Table 1

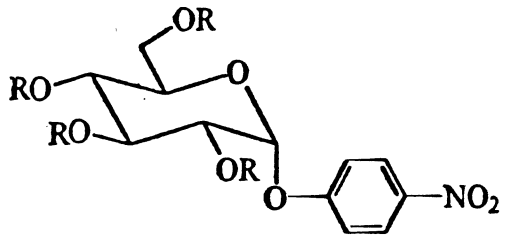
Number of Isomers of Sucrose Derivatives

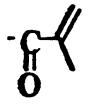
mono	8	penta	56
di	28	hexa	28
tri	56	hepta	8
tetra	70	octa	1

Whilst only one octaderivative of **1** can exist, there are 70 possible tetraderivatives and 56 alternatives in the case of both tri- and penta-derivatives. Selective acetylation of sucrose using 1.6 M equivalents of acetic anhydride has been claimed to give mono-O-acetylsucrose in 95% yield.[2] However, the product was not characterized and it is most likely a mixture of isomers. Treatment of **1** with 1.1 molar equivalents of acetic anhydride at -40 °C gave, after chromatographic separation, 6-O-acetylsucrose in 40% yield. Evidence for this structure has been provided by NMR.[3] Hough[4,5] has also reported that selected hydroxyls in sucrose can be chlorinated by exploiting the reactions with either sulphuryl chloride in pyridine or mesyl chloride in D.M.F.[6,7] With so many products formed, the yield of a particular isomer is very low. So while a few specific reactions do give reasonable laboratory yields of particular compounds, there exists no general method for the synthesis of specific derivatives of **1**.

Molecular recognition[8,9] might be the technique of choice to increase the

regioselectivity of some reactions of sucrose. Our goal is the synthesis of macroporous polymers using 4-nitrophenyl α-D-glucopyranoside **(2)** as a template from which a monomer, 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside **(3)** is prepared.



Compound	R
2	-H
3	

Hydrolysis of the template **2** from the polymer matrix would create glucose specific cavities. One of the ultimate possibilities we hope to accomplish is to carry out a regioselective reaction on sucrose bonded in the cavity.

B. MOLECULAR RECOGNITION AND SOLID PHASE SYNTHESIS

I. LITERATURE PREVIEW

When Linus Pauling[10] first postulated the template-and-cast theory in order to explain the ability of the human body's immune system to produce a large variety of specific antibodies, many scientists doubted his theory. Just recently many articles[8,10-16] have appeared in the literature where chemists are trying to exploit Pauling's template-and-cast strategy to create artificial equivalents of an anti-body that can recognize and isolate molecules with a very high selectivity.

During the last two decades, researchers such as Wulff,[8] Mosbach[11-16] and others [17-19] have struggled with the excruciatingly delicate task of custom-making a cast, or "imprint", of a desired template molecule, getting the right building blocks to assemble themselves around the template and then release the template so that the cast can recognize the template in the presence of other molecules. The overall scheme is outlined in Figure 1. A template molecule (T) is functionalized from three vinyl assemblies to give the monomer, which is then copolymerized with a large excess of cross-linking agent to give a three dimensional polymer matrix with T incorporated. Removal of the template leaves a cavity which can recognize the template molecule. The preparation of synthetic polymers with properties which mimic natural enzymes has been the aim of many research groups.[20-22]

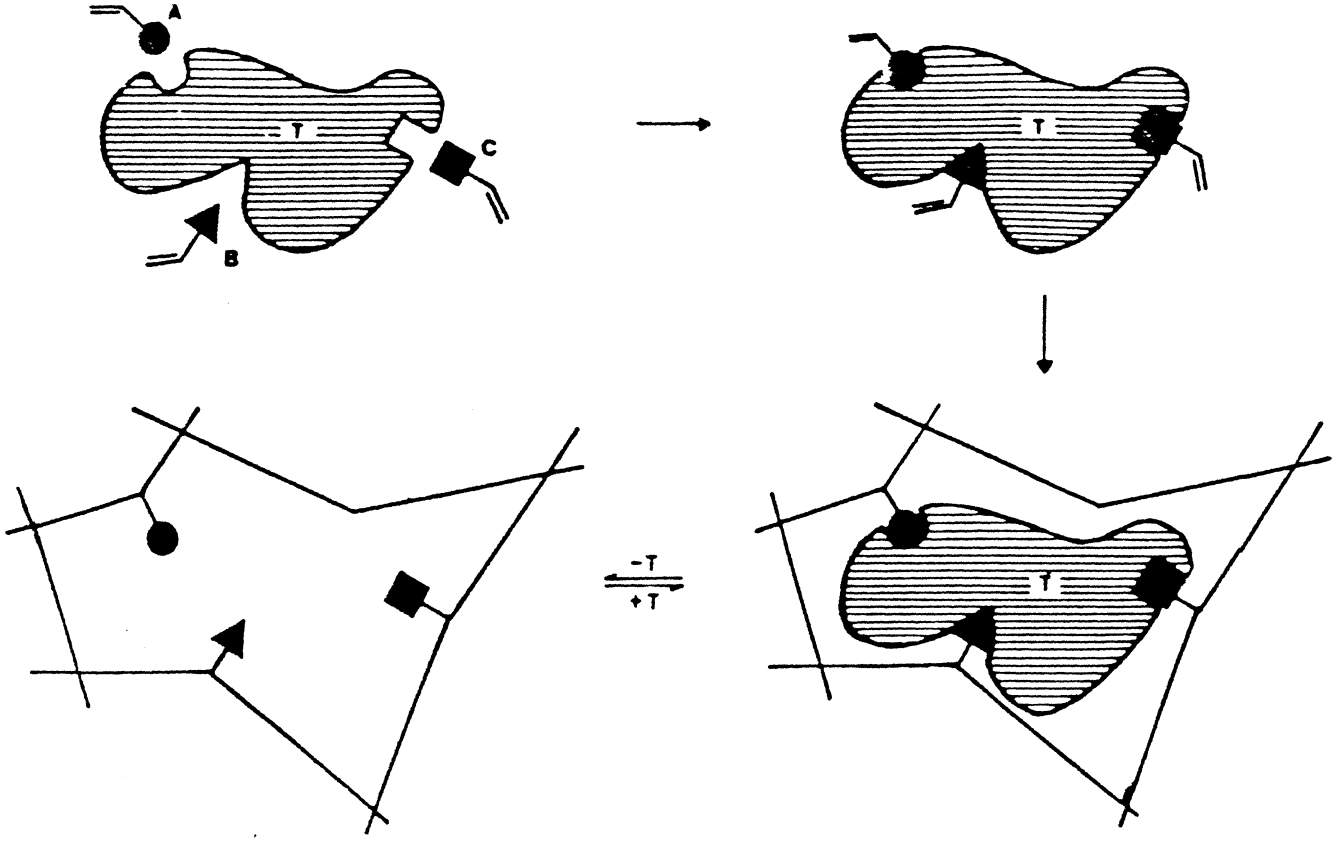


Figure 1:[3,10] Schematic representation of the imprinting process.

It is characteristic of the mode of action of enzymes that the substrate at first is specifically bound to the enzyme in a cavity containing a stereospecific arrangement of active groups,[8] followed by neighboring group catalysis of the bound substrate with another moiety or with the coenzyme attached to the enzyme. The last step is the desorption of the reaction product. For the specificity and activity of the enzymes, the form of the cavity and a specific arrangement of the functional groups involved in binding and catalysis is critical.[12,13]

The first step to an enzyme analogue, therefore, would be the preparation of synthetic polymers with specific cavities and functional groups therein, which possess a stereochemically exact, defined arrangement. In natural hormones and enzymes the functional groups responsible for the interaction with a receptor or a substrate can be arranged into two types, "continuate words" or "discontinuate words".[23] This is outlined in Figure 2.

Polymers of type A have been synthesized by the copolymerization of monomers resulting in a chain with randomly distributed groups. Another possibility is the grafting of side chains already containing the desired arrangement of functional groups onto a polymer, type B. A third possibility, type C, is the polymerization of monomers already containing the desired functional groups in the backbone. Here the groups are localized, as in some hormone receptors, in the main chain one after another, "continuate words". In contrast to these arrangements, in type D the functional groups responsible for the

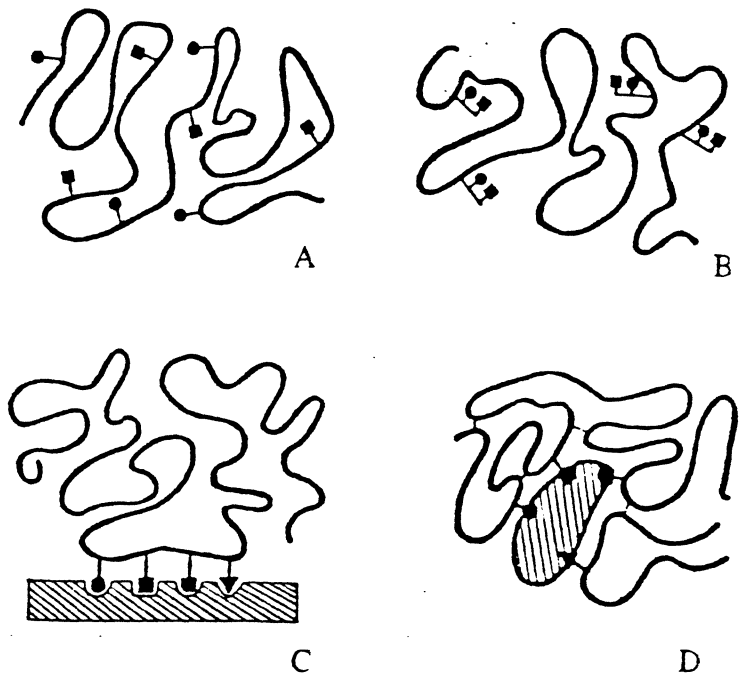
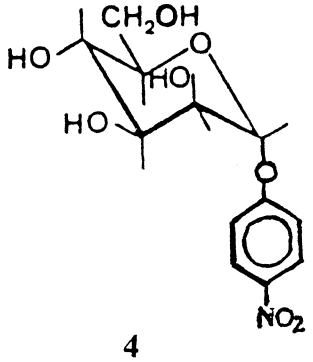


Figure 2: Polymer types A-D representing possible arrangements of functional groups in synthetic and natural polymers.[8]

specificity of natural enzymes are located at quite distant points along the peptide chain and are brought into spatial relationship as a result of the specific folding of the chain. This is referred as "discontinuate words" arrangement.[23]

Wulff[24-26]used phenyl α-D-mannopyranoside (**4**) as a template and synthesized the diborate ester (**5**) as a monomer. Copolymerization of **5** with a large amount of a

bifunctional crosslinking agent gave macroporous polymers[27-30] as shown in Figure 3.



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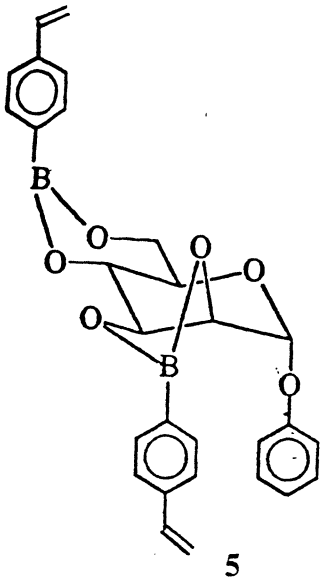


5

These polymers possess a permanent pore structure, a high surface area and good accessibility.[8] Treatment with water or alcohol on the template molecule removed 40-90% of the template molecule as shown in Figure 4. When this polymer was treated with a racemate of the template,[25,26] one of the enantiomers, the one used for the preparation of the polymer, was preferably incorporated. For the characterization of the specificity of the polymers the separation factor α was used. This represents the ratio of the distribution coefficients between solution and polymer of the L- and D-forms. This is shown in equation 1-1.

$$\alpha = K_D/K_L \qquad (1\text{-}1)$$

The distribution coeficient K_D is defined as:

$$K_D = c_{p\ Mann}/c_{s\ Mann} \qquad (1\text{-}2)$$

where $c_{p\ Mann}$ = equal concentration of mannoside **4** on the polymer (in mol dm^{-1}) and $c_{s\ Mann}$ = concentration of mannoside **4** in solution (in mol dm^{-1}). Values of α in this and

other cases ranged from 1.20 to 3.66, depending upon the equilibration conditions and polymer structure.[24,28] The high specificity obtained for optical resolution showed that it was indeed possible to introduce functional groups into a polymer in a "discontinuate words"[14] arrangement analogous to that in enzymes.

Molecularly imprinted polymers[9] are increasingly being recognized as specialized separation media especially in High Performance Liquid Chromatography (HPLC), in applications such as enantiomeric separations.[16,30] Important examples include resolution of amino acid derivatives[31,32] and direct enantioseparation of drugs,[33,35] for example ß-

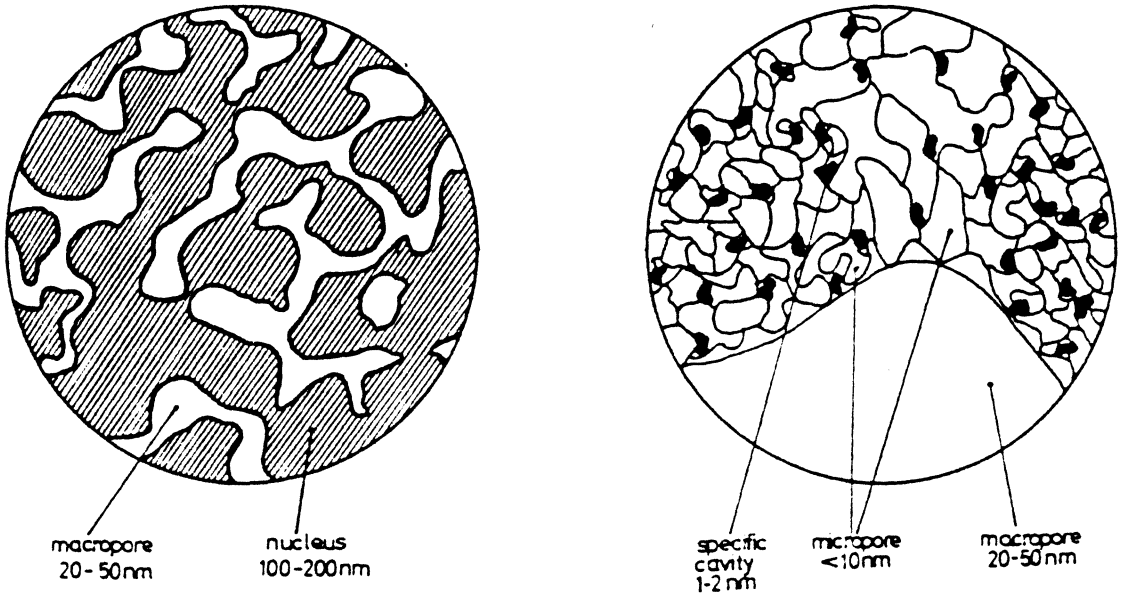


Figure 3: Schematic diagrams of a macroporous polymer with chiral microcavities at two magnifications.[8]

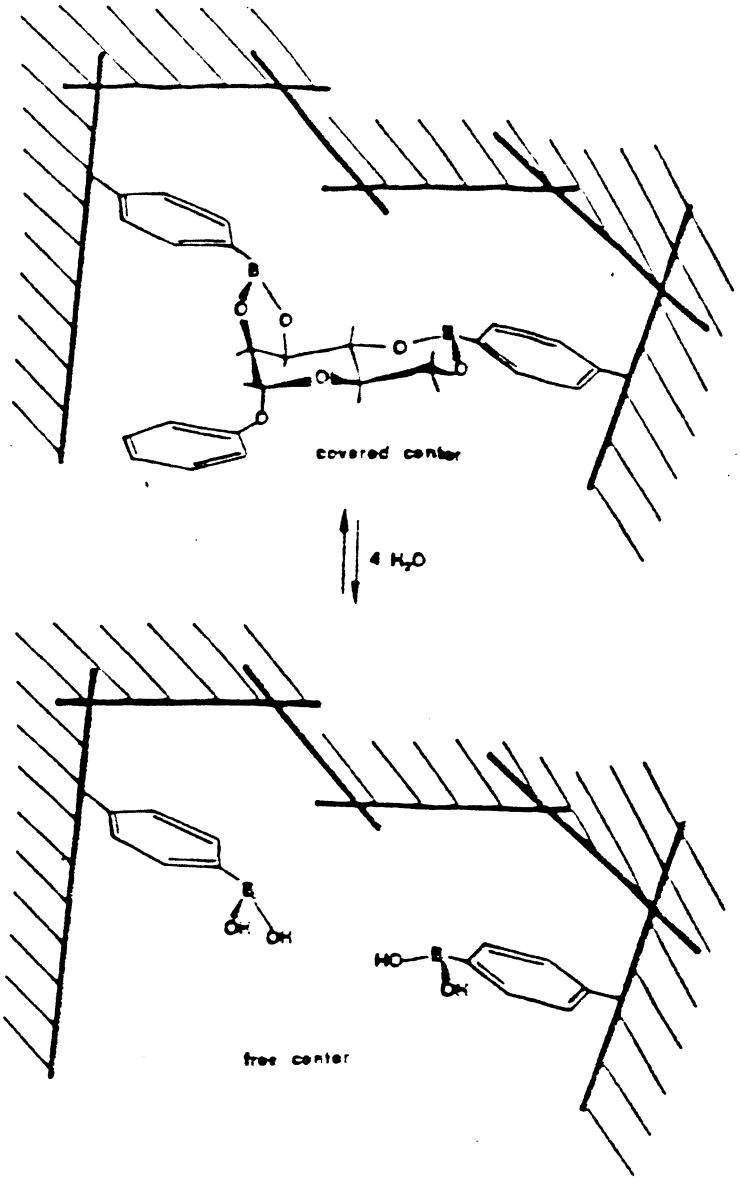
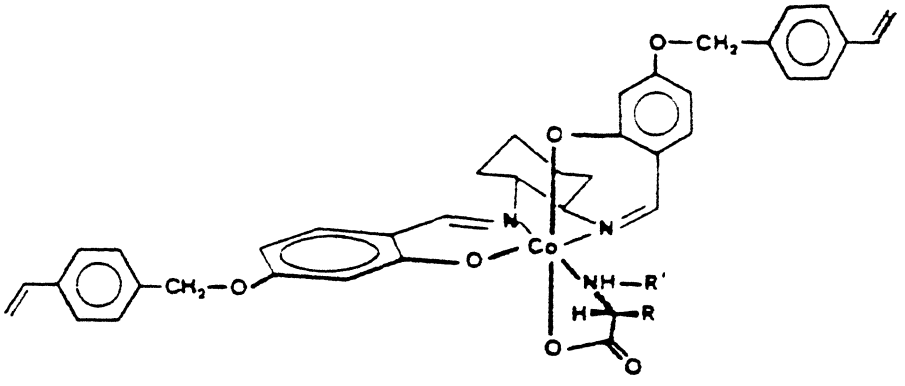


Figure 4:

Removal and uptake of the template.[8]

adrenergic blockers.[36] An extremely efficient optical resolution of D,L-N-benzylvaline was reported by Fugii and coworkers.[37] They used the amino acid Schiff base Cobalt (III) complex **6** as the template monomer.[38]

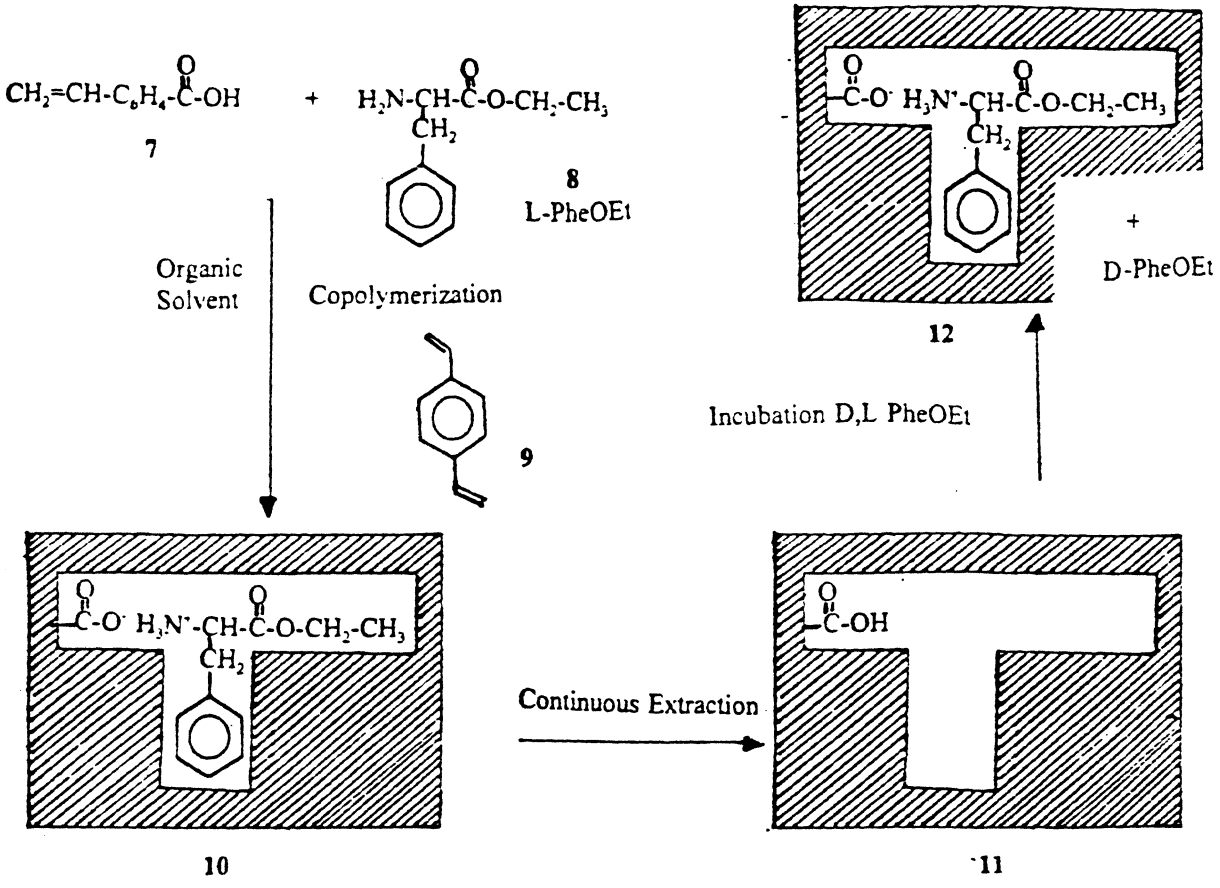


6

After splitting off the template from the crosslinked polymer, the polymer showed preference of the L isomer and a selectivity of $\alpha = 682$ was achieved.

Rather than using covalently bonded polymerizable groups, Mosbach[11,39]prepared L-phenylalanine-ethyl ester-selective polymers using the ion pair association between template and carboxyl containing monomers. This is shown in Scheme 1.

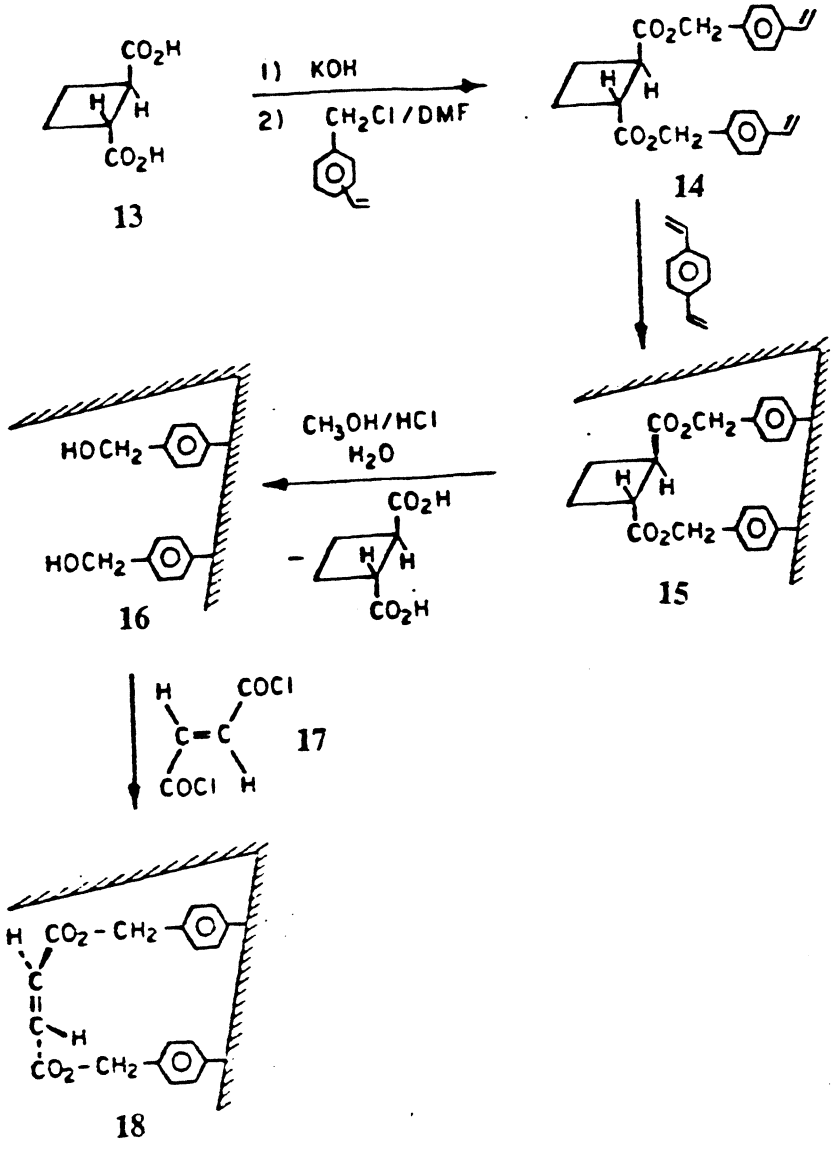
Paravinylbenzoic acid (**7**) is polymerized with divinylbenzene (DVB) (**9**) to form **10**. During polymerization the substrate molecules interact with the carbonyl containing vinyl monomers due to the columbic attraction between the opposite charges. After



Scheme 1: Preparation of phenylalanine ethyl ester-selective polymers

polymerization, the template was washed away and the imprinted polymer could still recognize the print molecule. A selectivity of α=1.04-1.08 was achieved.

Shea[17,40-43] has synthesized several copolymers by the template synthesis method. The divinyl monomer **14** was synthesized[17] and then subjected to radical polymerization

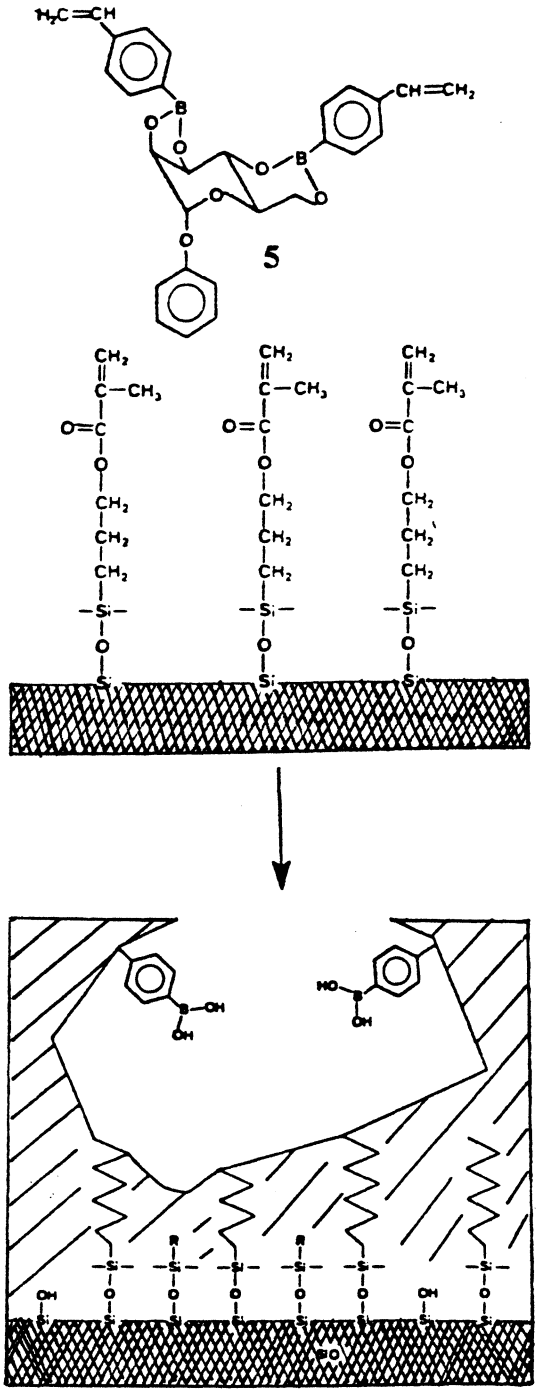


Scheme 2: Synthetic route for the formation of macroporous polydivinylbenzene copolymers of bis(vinylbenzyl) *trans*-1,2-cyclobutanedicarboxylate (14).[17]

conditions in the presence of toluene or acetonitrile as inert diluent. High surface area polymers were obtained which were then subjected to hydrolysis conditions to split out the template. This is shown in Scheme 2. In both cases the template was liberated in an overall yield of 34%.

Rebinding experiments with a difunctional reagent, fumaryl chloride **(17)** of similar geometry to the template molecule, *trans*-1,2-cyclobutanedicarboxylic acid **(13)** suggests that the benzyl alcohol functional group retains some of the information originally present in the cyclobutane diester. The rebinding occurs by the formation of new ester linkages between the polymer and the fumarate group.

An alternative procedure for the preparation of substrate-selective polymers using high surface area and wide pore silicas was been reported.[11,44] In this procedure the silica surface was modified by 3-(trimethoxysilyl)propyl methacrylate by formation of siloxane bonds. To such a silica, layers of approximately 50-100 Å thickness of a monomeric mixture of **5** were radically polymerized. The template molecule was later cleaved from the modified silica as illustrated in Scheme 3. The silicas after coating were still macroporous. The template could be nearly completely removed by hydrolysis.

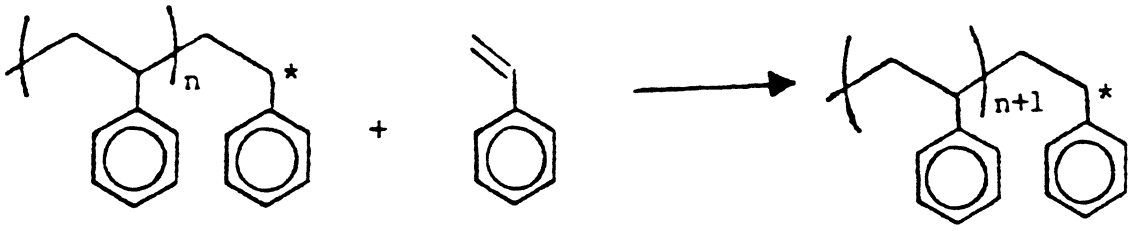


Scheme 3: Schematic picture of polymer coated silica imprinted by 5 and its hydrolysis from the polymer matrix

II. POLYMERS AND POLYMERIZATION

a) Polymer Synthesis

Most polymerization reactions fall into two large classes, chain growth and step growth polymerizations. Chain growth polymerization is shown in Scheme 4.



22 23 24

* = , + , -

Scheme 4 Chain Growth Polymerization

In a chain growth process a macromolecule is formed rapidly from monomer *via* a highly reactive intermediate such as a free radical, a carbanion, a carbocation or a transition metal alkyl complex. After partial conversion of monomer in a free radical polymerization, the reaction mixture contains monomer and high molecular weight polymer. A step growth polymerization involves slow reactions of two monomers to form dimer, dimer and monomer to form trimer, two dimers to form tetramers, and so on in all possible combinations until macromolecules are formed. High molecular weight is achieved only after high conversion of monomer. After partial conversion, the reaction

mixture contains a broad distribution of monomers and oligomers.

The experimental conditions for chain growth polymerization normally require exclusion of all contaminants that may react with the free radical, carbanion, carbocation and transition metal alkyl intermediates. Oxygen, water, carbon dioxide and many other compounds can stop the chain reactions. Polymerizations are usually carried out under rigorous inert atmosphere conditions. Free radical processes are generally the easiest to execute because only oxygen needs to be excluded and have been the preferred type in investigations of molecular imprinting.

The most common supports for polymeric reagents are produced by free radical copolymerization of a vinyl monomer such as acrylonitrile, 4-vinylpyridine, or 3- and 4-chloromethylstyrene with a crosslinking agent such as divinylbenzene **(9)**.[45,46] Uniform distribution of the functional sites on a microscopic level occurs only if the copolymerization is nearly random rather than alternating.

Free radical polymerization processes are carried out in bulk, solution, suspension, emulsion, or by precipitation techniques.[47] Bulk and solution polymerizations produce solid and precipitated plastics that are ground into irregularly-shaped particles of the desired size. Suspension polymerization of droplets of monomers dispersed in water with an oil soluble initiator produces spherical polymer beads whose particle sizes depend on the condition of the synthesis.

Suspension polymerization is, unfortunately, by no means as straightforward as it might first appear, since the physical form of the products depends crucially on the polymerization conditions.[47] This includes such details as the vessel shape, the stirrer size and shape, the stirring speed and the types and concentrations of suspending agents. The optimum conditions for a particular monomer mixture must often be determined by trial and error, though once found the polymerizations are usually reproducible without difficulty. By selecting appropriate conditions microporous or macroporous polymer beads can be obtained.[47] The former are prepared using low levels of crosslinking agent. When the product is dried the polymer matrix collapses to give beads with only very small pores (micropores). Macroporous polymers on the other hand are usually prepared using relatively large amounts of crosslinking agent. Macroporous polymers are relatively rigid. When they are dried, the matrix does not collapse and the large pores remain.

Macroporous polymers as shown in Figure 3 consist of primary particles (so called nuclei) grown together during polymerization. Electron micrographs[17] show macroporous polymers to be agglomerates of randomly packed microspheres. The voids between these microspheres comprise a network of channels similar to that those found in bone char or alumina.[41] In polymers that contain a high mole fraction of cross-linking agent, these voids are a permanent skeletal feature and do not collapse upon removal of solvent.

b) Mechanism of Vinyl Polymerization

The process of vinyl polymerization as a chain mechanism dates back to the work of Staudinger[48] in 1920. In 1937 Flory[49] showed that radical polymerization proceeds by and requires the steps of initiation, propagation and termination typical of chain reactions in low-molecular-weight species. The carbon-carbon double bond, because of its relatively low stability, is susceptible to attack by a free radical. The reaction of the double bond with a radical proceeds well for compounds of the type $CH_2=CHX$ and $CH_2=CXY$, called vinyl monomers.

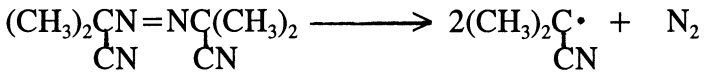
Organic reactions take place through intermediates having an odd number of electrons and an unpaired electron. Such intermediates are known as free radicals and they can be generated in a number of ways, including thermal decomposition of organic peroxides, hydroperoxides, azo and diazo compounds.

The most common initiators are either acyl peroxides, hydroperoxides, or azo compounds. Hydrogen peroxide, potassium persulfate and sodium perborate are popular in aqueous systems. Two most commonly used reactions to produce radicals for polymerization are the thermal or photochemical decomposition of benzoyl peroxide **(25)**,

$$(C_6H_5COO)_2 \longrightarrow 2C_6H_5COO^{\cdot} \longrightarrow 2C_6H_5^{\bullet} + 2CO_2$$

25 **26** **27**

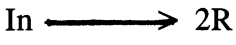
and of azobisisobutyronitrile **(28)** (AIBN),

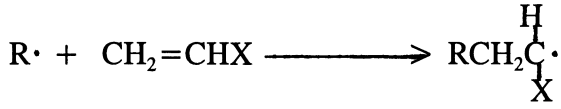


28 **29**

Initiation:

When free radicals are generated in the presence of a vinyl monomer, the radical adds to the double bond regioselectively with the generation of another radical. The radical formed by decomposition of the initiator In is designated by R•.





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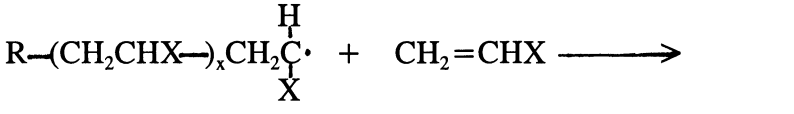
Propagation:

The radical formed in the initiation step is capable of adding successive monomers to propagate the chain:



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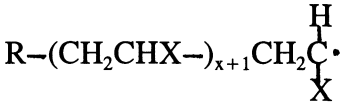

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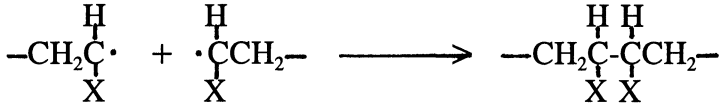
Termination:

The termination step can take place when two radicals react in pairs to form a radical paired-electron covalent bond with loss of radical activity.



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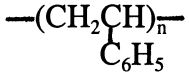
c) Polymer structures and properties

Synthetic polymers are families of chains composed of different numbers of structural units, thus differing in molecular weight. Thus, polystyrene has the repeat unit structure **34**



34

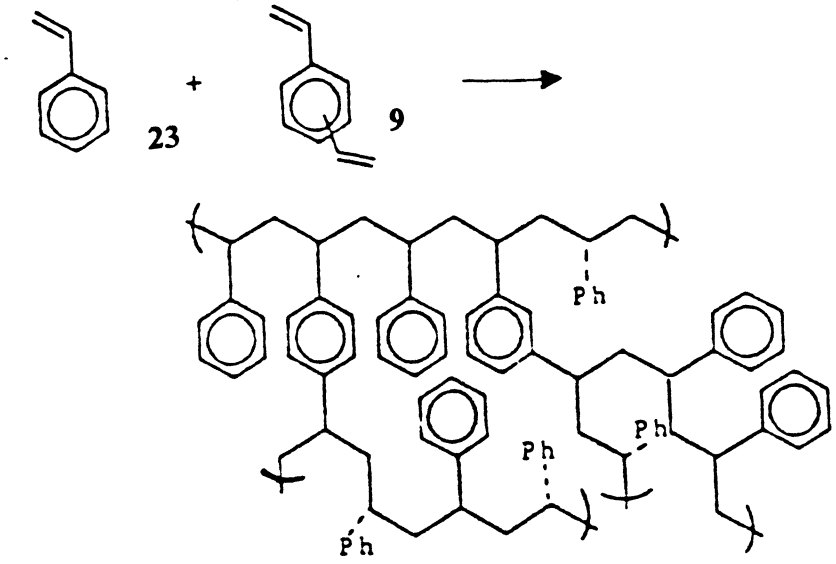
where n is the average degree of polymerization or the average number of repeat units per molecule. A polymer is made by polymerization of monomer, a small molecule that reacts in a regular, repeating fashion.

A copolymer is a polymer made from two or more different monomers. Those repeat units, A and B as shown in Figure 5 may be arranged in alternating, block or random fashion.

ABABABABABABABABABAB	alternating
AAAAAAAAAABBBBBBBBBB	block
ABBABBBBABABBBBAAABA	random

Figure 5: Possible arrangements of monomers in a copolymer

Macroporous polymers are totally insoluble when they are cross-linked by bonding the primary macromolecular chains into a network. Copolymerization of styrene (**23**) with divinylbenzene (**9**) provides the cross-linked polymers frequently used for polymer supported reagents and catalysts as shown in Scheme 5. The insolubility of macroporous polymers makes them easy to separate from a reaction mixture but complicates their analysis. The molecular weight of a highly crosslinked polymer is effectively infinite. A solvent that dissolves a linear polymer only swells a cross-linked polymer. Some swelling of a polymeric reagent is usually necessary to permit transport of the reagents to the reactive sites within the polymer network.



Scheme 5: Copolymerization of styrene and divinylbenzene

d) Reactivity Ratios

If there are two monomers M_1 and M_2, they lead to radicals $M_1^{\bullet}$ and $M_2^{\bullet}$. There are four possible ways in which these radicals can add to the momomers:[50]

Reaction	Rate	
$M_1^{\bullet} + M_1 \xrightarrow{k_{11}} M_1\text{-}M_1^{\bullet}$	$k_{11}[M_1^{\bullet}][M_1]$	(1-3)
$M_1^{\bullet} + M_2 \xrightarrow{k_{12}} M_1\text{-}M_2^{\bullet}$	$k_{12}[M_1^{\bullet}][M_2]$	(1-4)
$M_2^{\bullet} + M_1 \xrightarrow{k_{21}} M_2\text{-}M_1^{\bullet}$	$k_{21}[M_2^{\bullet}][M_1]$	(1-5)
$M_2^{\bullet} + M_2 \xrightarrow{k_{22}} M_2\text{-}M_2^{\bullet}$	$k_{22}[M_2^{\bullet}][M_2]$	(1-6)

The rate of conversion of $M_1^{\bullet}$ to $M_2^{\bullet}$ must equal that of conversion of $M_2^{\bullet}$ to $M_1^{\bullet}$, assuming that a steady state exists so that the concentration of $M_1^{\bullet}$ and $M_2^{\bullet}$ remain constant:

$$k_{21}[M_2^{\bullet}][M_1] = k_{12}[M_1^{\bullet}][M_2] \qquad (1\text{-}7)$$

The rates of disappearance of the two types of monomers are given by

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^{\bullet}][M_1] + k_{21}[M_2^{\bullet}][M_1] \qquad (1\text{-}8)$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^{\bullet}][M_2] + k_{22}[M_2^{\bullet}][M_2] \qquad (1\text{-}9)$$

By defining $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ and combining equations 1-7, 1-8 and 1-9, it can be shown that the composition of copolymer being formed at any instant is given by

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\ r_1[M_1] + [M_2]}{[M_2]\ [M_1] + r_2[M_2]} \qquad (1\text{-}10)$$

This equation is known as the copolymer equation.[50] A copolymer system is said to be ideal for a particular reaction when the two radicals $M_1^{\bullet}$ and $M_2^{\bullet}$ show preference for adding one of the monomers over the other.[50] Monomer reactivity ratios r_1 and r_2 are the ratios of the rate constants for a given radical adding its own monomer to that for adding the other monomer. Thus $r_1 > 1$ means that the radical $M_1^{\bullet}$ prefers to add M_1 ,

Table 2:

Some Typical Monomer Reactivity Ratios[50,51]

Monomer 1	Monomer 2	r_1	r_2	T°C
Acrylonitrile	1,3 Butadiene	0.02	0.3	40
	Methyl Methacrylate	0.15	1.22	80
	Styrene	0.04	0.4	60
	Vinyl acetate	4.2	0.05	50
	Vinyl chloride	2.7	0.04	60
Methyl Methacrylate	Styrene	0.46	0.52	60
	Vinyl acetate	20	0.015	60
	Vinyl chloride	10	0.1	68
Styrene	Vinyl acetate	55	0.01	60
	Vinyl chloride	17	0.02	60

$r_1 < 1$ means that it prefers to add M_2 . When $r_1 = r_2 = 0$, an alternating copolymer

is formed. Reactivity ratios are unaffected by the presence of inhibitors or solvents. A few typical values of monomer reactivity ratios are given in Table 2.[50,51]

The choice of the right polymerizable units on the monomers being considered to react is a very important consideration during copolymerization. A random copolymer distribution is very desireable in our research since it closely mimics the enzyme analogue. The "discontinuate words" pattern as illustrated in Figure 2, polymer type D, was chosen as our model, thus in order to have a random copolymer distribution similar to this model the reactivity ratios of styrene, DVB and methyl methacrylate have to be very similar.

IV. Analysis of Polymers

Monitoring reactions of polymers is not always easy, especially when the polymer is crosslinked and therefore insoluble. Various techniques have been used. They all have their limitations and to be confident of drawing the correct conclusions for any reaction it is wise to use a combination of techniques. The mostly widely used techniques are outlined below.[52]

1. Elemental Analysis: Although carbon and hydrogen analyses are often carried out routinely this technique is most useful when such an element such as nitrogen, halogen, sulphur or phosphorous is gained or lost in the reaction.

2. Titration of reactive groups: Polymer-bound groups such as acids, phenols, bases, oxidizing agents can be titrated by the usual methods.

3. Infrared spectroscopy: This is a vital method for following the course of the reactions of polymers. All the usual characteristic infrared bands are useful. The sensitivity of the method has been enhanced by the introduction of Fourier transform infrared spectrometers, particularly by their ability to measure difference spectra.

4. Nuclear magnetic resonance spectroscopy: ^{1}H and ^{13}C NMR spectroscopy are highly useful for soluble polymers[53] and in some cases they can provide valuable information on the sequence in copolymers.[54] NMR spectra can often be used to identify the distribution of microstructural sequences in copolymers and stereochemical microstructures of polymers with pseudochiral carbon atoms in the main chain. Low levels of structural defects and end groups can sometimes be identified. NMR is very difficult but can still be used with crosslinked polymers.[55] Lightly crosslinked, highly swollen gels by liquid state techniques give definitive ^{13}C spectra whose lines are typically ten times wider than those of low molecular weight organic compounds. Similar line broadening causes so much overlap of the lines in ^{1}H spectra that the spectra are not useful. Solid-state NMR is expected to greatly assist in monitoring reactions in the near future.

5. Molecular weight determination: These determinations are only meaningful for linear polymers. They can provide information on polymer degradation by chain scission or on

crosslinking reactions.

6. BET Surface Area Analysis: This technique is used to determine the surface area of a sample by employing the techniques of adsorbing the adsorbate gas from a flowing mixture of adsorbate and an inert non-adsorbable carrier gas. The following operational BET equation **(1-11)** is used to calculate the total surface area of a sample. The total surface area is divided by the mass of the sample in order to calculate the surface area per gram.

$$S_t = (1-P/P_o)\,(A/A_c)\,V_c \frac{NA_{cs}\,P_a}{RT}\ m^2 \qquad (1\text{-}11)$$

P = Partial pressure of adsorbate P_o = Saturated pressure of adsorbate

N = Avogadro's number = 6.023×10^{23} R = Gas constant = 82.1cc atm/°K Mole

V_c = Volume of calibration P_a = Ambient pressure, atm

A = Signal area A_c = Area of calibration

A_{cs} = Cross sectional area of adsorbate molecule in square meters for N_2, $16.2 \times 10^{-20}\ m^2$

T = Temperature of calibration volume in degrees Kelvin

7. Other techniques: These include electron spin resonance spectroscopy and thermal analysis.[56,57]

CHAPTER 2

RESULTS AND DISCUSSION

The ultimate goal of our research is to apply the results of studies of molecular recognition[8,9] by template imprinting to the creation of a material that would "recognize" and bind to sucrose in such a way as to block certain of the hydroxyl groups.
The following sequence of steps as outlined in the original research proposal shows important stages we have to accomplish towards our ultimate goal:

a) using an α-D-glucopyranoside as a template, design and synthesize an appropriate monomer molecule,

b) use the monomer to prepare the polymer, thus creating a glucose specific cavity,

c) remove the template molecule from the polymer cavity,

d) bind sucrose to the polymer cavity

e) characterize the polymer/sucrose adduct

f) demonstrate that the bound sucrose can be removed from the polymer

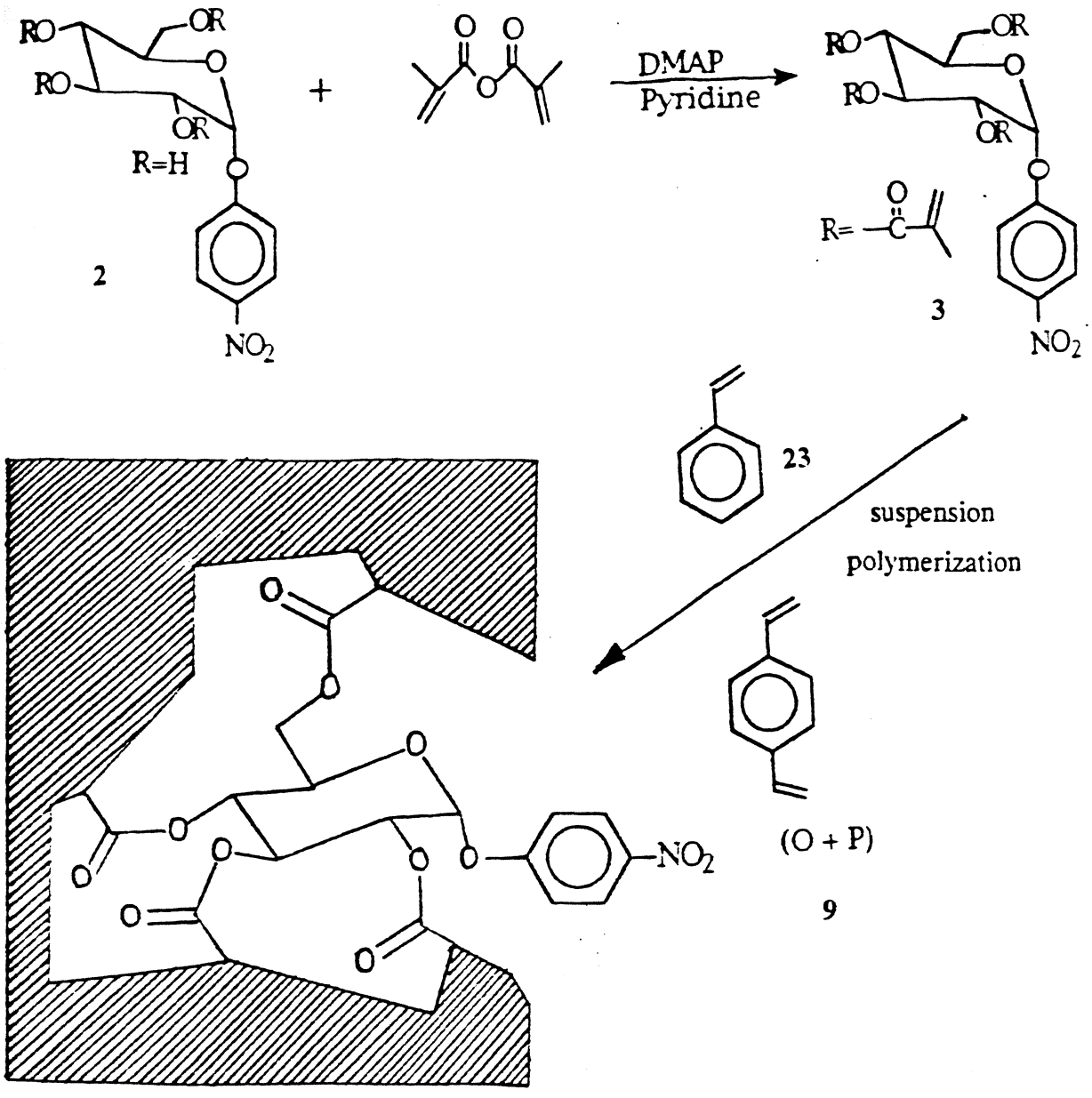
g) evaluate the regioselectivity of a series of reactions with the bound sucrose

A detailed account of step a), the choice of the template, its functionalization to form the monomer, synthesis and characterization is given by Jiang.[58] This thesis deals with step b). Progress at this initial stage is very crucial for the success of succeeding steps. We proceeded to use 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside **(3)** as the monomer. The monomer was then copolymerized by free

radical initiation in the presence of an "inert" solvent such as toluene or benzene, with styrene **(23)** using divinylbenzene **(9)** as a crosslinking agent. A milky white polymers was formed which was observed under the microscope as randomly shaped particles although some of these macroporous polymers were found to be spheres of random sizes.

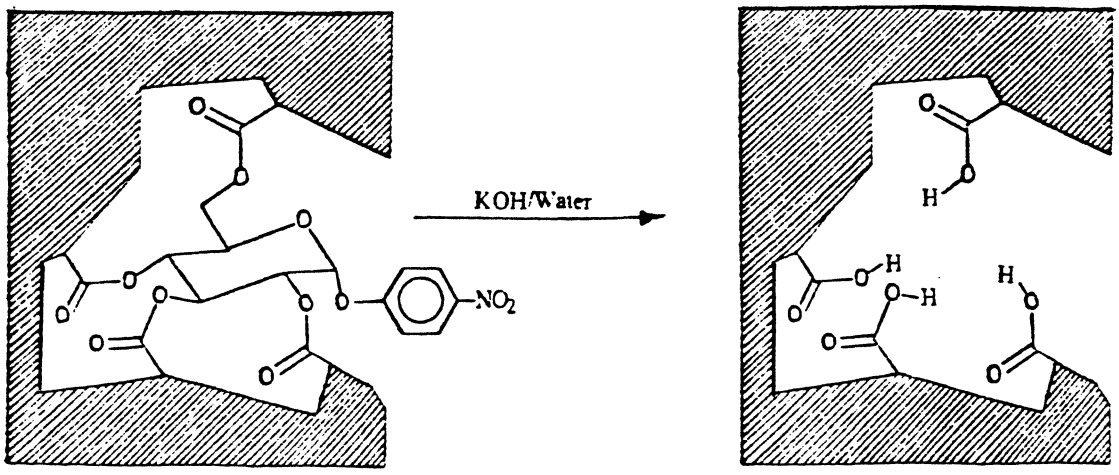
The most common procedure for polymerizing water insoluble monomers involves suspension polymerization and bulk polymerization. We employed suspension polymerization because of its simplicity and low cost and it is more appropriate for industrial settings. Different solvents were used as shown in Table 3. The percentage of crosslinking and the mole fraction of the monomer was also varied in order to find suitable conditions for macroporous polymer synthesis.

All the copolymers of **3** exhibit the ester carbonyl stretching frequency at about 1736 cm^{-1} and the strong band for the C-O-C stretching vibrations around 1165 cm^{-1}. The lack of absorption for conjugated C=C stretching band at 1635 cm^{-1} suggests that there are no detectable conjugated vinyl groups in the polymer. However, the use of it for this application has been questioned by Ford.[59] Monomer **3** has the nitro group which acts as an analytical indicator for the presence of the monomer in the polymer. The presence of the nitro stretching frequencies at 1490 and 1335 cm^{-1} is an indication that the monomer has been incorporated. Other bands present in the polymers include the aromatic C=C bands at about 1603, and 1447 cm^{-1}.



Scheme 6: The synthetic route for the synthesis of 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside and macroporous polymers

Preliminary studies hydrolytic removal of the template as shown in Scheme 7 are not conclusive at the present moment. TLC analysis of the hydrolysis filtrate did not show the presence of the template although this technique is not very sensitive. UV-Vis analysis of this basic filtrate seems to show the presence of the 4-nitrophenoxide ion with λ_{max} = 398nm and the template with λ_{max} = 300nm. An explanation to this might be that a significant number of template assemblies occupy regions that are inaccessible to the



Scheme 7: Hydrolysis of 2

reagents used. These template assemblies might be buried in the interior of the highly cross-linked nucleus of polydivinylbenzene and might be inaccessible to chemical reagents. Alternatively the low extent of hydrolysis may be the result of a kinetic barrier to hydrolysis because of the hydrophobic environment of the ester group.

The copolymers in Table 3 are prepared with a low mole fraction of template monomer (0.85-5%) to divinylbenzene **(9)** (DVB). We reasoned that at these low levels, the template assembly would not make a significant contribution to the whole structural rigidity of the polymer so that after removal of the template the polymer matrix would not collapse and change the shape of the cavities.[17] However these low mole percentages of the monomer result in low numbers of functional groups and this presents a difficult problem for characterization by the various analytical methods available.

The polymers described in this work are prepared from a technical grade of divinylbenzene which consists of a mixture of meta and para isomers of ethylvinyl-benzene and **9** (45:55) together with a trace of ($<1\%$) of *meta* and *para* diethylbenzene . Polydivinylbenzene formed by free radical initiated polymerization of styrene and divinylbenzene is a brittle, glassy, amorphous substance that is insoluble in organic solvents and is chemically inert. Our choice of DVB was influenced by its reactivity ratio and availability as well as low cost. DVB provides the structural rigidity to the polymers necessary to preserve the polymer cavities after splitting off the template. In contrast to the requirement for rigidity the polymers should also possess some flexibility in their whole arrangement. This is necessary to allow a fast binding to and removal of the substance within the cavities. The cavities should not change their shape during diffusion and rebinding of template; thus DVB seems to be the right choice since it's a short molecule and ensures that the polymer cavities are rigid.

Table 3: Analytical Data of Macroporous Polymers

Polymer Number	Solvent	% Crosslinking[A*]	% of Monomer[B*]	% Yield[C*]	Surface Area[D*] (m^2/g)
1	benzene	55	0.00	46	1302
2	benzene	55	0.85	89	528
3	benzene	35	0.85	70	4
4	benzene	25	0.85	60	3
5	benzene	55	5.00	57	85
6	toluene	55	0.00	62	537[E*]
7	toluene	35	0.85	78	1
8	toluene	55	2.76	72	487
9	toluene	55	2.76	79	739[E*]
10	toluene	55	3.31	89	712
11	THF	55	0.00	56	421
12	THF	55	0.85	65	1365
13	THF	55	3.16	44	0.2[F*]
14	THF	55	5.00	82	1045
15	acetonitrile	55	0.00	79	114
16	acetonitrile	55	0.00	70	97[E*]
17	pyridine	55	0.00	83	39
18	pyridine	55	0.85	73	145

A* Based on mole % of divinylbenzene, B* Mole % of monomer in the polymer, C* Calculated as mass % yield, D* % error 10-12%, E* Refers to polymers prepared by method B, F* Starch substituted for gelatin during polymer preparation.

CHAPTER 3

CONCLUSIONS

A monomer with four polymerizable units was prepared and copolymerized with styrene and divinylbenzene to form a three-dimensional cross-linked polymer. Based on current evidence, essentially all of the monomer was incorporated. We have prepared eighteen polymers using different solvents during each preparation and we learned that different reaction solvents results in polymers of different surface areas. The best solvents which give very high surface areas are THF and benzene, whilst pyridine gave the least surface area. There is a very noticeable decrease in the surface areas of most polymers when the percentage crosslinking is decreased from 55% to lower values. There seems to be less difference in the surface areas of polymers made by method A to those made by method B. When gelatin was used instead starch during the polymerization process, we noticed a very significant change in the surface area of the polymers although it not very clear why this occurs. The effect of mole percentage of monomer **3** on the surface areas appeared to be mostly random. The yield of the polymers were generally quite good. Hydrolysis studies to cleave the template and create glucose specific cavities are incomplete.

In summary, we have established an efficient and cheap method to make macroporous polymers with very high surface areas in satisfactory yields.

EXPERIMENTAL SECTION

A. General Methods and Instrumentation

Melting points were measured with a Fisher-Jones Melting Point Apparatus and were uncorrected. Infrared spectra were recorded on a Nicolet 20DXB FTIR spectrophotometer and only the major absorptions are cited. ^{1}H-NMR spectra were recorded on a 300 MHZ General Electric QE 300 instrument using tetramethylsilane (TMS) as an internal standard. BET single point analysis was carried out using a "Quantasorb" Quantachrome Analyzer with 0.300 mole fraction of nitrogen in helium. Degassing was done at 120 °C for about 3 hours. UV-Vis analysis was done with a Shimadzu UV spectrophotometer UV-160A using methanol as the solvent.

Column and flash chromatography was carried out with Fisher Silica Gel S-704 60-200 Mesh. All the inhibitors in styrene and divinylbenzene were removed by running the reagent through a 2 cm column of alumina prior to the reaction. All reactions requiring anhydrous conditions were performed under a positive pressure of nitrogen.Thin Layer Chromatography (TLC) was performed using Analtech 250 microsilica gel plates. The template starting material **2**, used for the preparation of monomer **3**, was purchased from Aldrich Chemical Company (Milwaukee) and was used without further purification. Divinylbenzene **(9)** was purchased from Aldrich. The term divinylbenzene (DVB) refers to the commercially available material which is 55 % mixture of *meta* and *para* isomers and 45 % mixture of *meta* and *para* isomers of

ethylvinylbenzene.

General Preparation of KBr Pellets

A mull of the macroporous polymer and KBr was prepared in a mortar with a pestle. An average of 200-250 mg of the mull was added into a die assembly that was placed in a hydraulic press. It was subjected to 4000 pounds of pressure for about 2 minutes, after which the die was removed and disassembled. All FT-IR spectra were recorded as KBr pellets.

B. Procedures

Preparation of 4-Nitrophenyl 2,3,4,6-tetra-O-methacroyl-α-D-glucopyranoside (3)[59]

In a 150-mL Erlenmeyer flask, 4-nitrophenyl α-D-glucopyranoside **(2)** (0.58 g, 1.94 mmol) was dissolved in 50 mL of previously dried pyridine. To this mixture was added 4-dimethylaminopyridine (0.043 g, 0.351 mmol) and methacrylic anhydride (2.9 mL, 19.4 mmol). The suspension was stirred in an ice-bath until **2** dissolved. Stirring was continued in the dark at room temperature for 48 hours. The mixture was then poured with stirring into a beaker containing a mixture of ice and water. Then 15 mL of ether was added with stirring and the aqueous layer was twice extracted with 10 mL of ether. The ether layers were combined, washed once with water then sulphuric acid until acidic, then with sodium bicarbonate until basic and again with water. The ether solution

was dried over magnesium sulphate for 24 hours. Magnesium sulphate was then filtered off and the solvent evaporated to give a white solid. Recrystallization from 95% ethanol yielded 0.67 g (1.168 mmol, 61%) mp. 174-175 °C; FT-IR and ^{1}H-NMR (DMSO-d_4) spectral data are identical to those given by Jiang.[59]

General method for copolymer preparation

All the polymers were prepared by either method A or B. The solvent and the amounts of monomer, cross-linking agent used were varied in each case as summarized in Table 3.

Copolymer 4-Nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside.

Method A.

A 250-mL 3-neck round bottomed flask was fitted with a reflux condenser, mechanical stirrer and a thermometer. Gelatin (2.00 g) was dissolved in 130 mL of water and heated to 65 °C, then was allowed to cool to room temperature. A solution was prepared containing styrene, divinylbenzene (DVB), 50 mL solvent, AIBN (2,2'-azobis (2-methylpropionitrile)) and monomer **3**. This solution was slowly added to the stirring gelatin solution at an even rate for about 10 minutes. The temperature was gradually brought to temperatures indicated for each polymer. The reaction mixture was stirred at a constant rate of 350 RPM with a mechanical stirrer for 24 hours. A positive nitrogen

pressure was maintained throughout the course of polymerization. The polymer was filtered, washed three times with water then with acetone in a Buchner funnel and then extracted with acetone overnight in a Soxhlet apparatus. The acetone extract was examined by TLC and ^{1}H-NMR to detect if there were any traces of unreacted styrene, divinylbenzene or monomer. The polymer was then dried to constant weight under vacuum at 100 °C in an Abderhalden apparatus.

Copolymer p-Nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside. Method B.

A solution containing DVB, AIBN, 2.5 mL of solvent and monomer **3** was placed in a medium-walled glasstube which had a constricted neck for sealing. The tube was degassed under a vacuum through five consecutive freeze-thaw cycles before being sealed, covered with a wire gauze, and placed in an oil bath where it was incubated at the indicated temperatures for the times listed. The polymer was ground up with a mortar and pestle. The polymer was sized up by sieving. Fractions of 60-120 mesh (75-250 μ) and $<$ 200 mesh ($<$ 75 μ) were collected. These were washed in the Soxhlet extractor with acetone overnight. The acetone extract was examined by TLC and ^{1}H-NMR to detect if there were any traces of unreacted styrene, divinylbenzene or monomer. The polymer was then dried to constant weight under vacuum in an Abderhalden apparatus.

Preparation of Polymers 1-18.

All polymers were prepared by method A except polymers 6, 9 and 16.

Blank copolymer of styrene and divinylbenzene. Polymer 1.

A solution containing DVB (2.45 g, 18.82 mmol), styrene (0.245 g, 0.2353 mmol), 50 mL benzene and AIBN (0.100 g, 0.7343 mmol) was prepared. The temperature was gradually brought to 80 °C. The weight of the macroporous material was 1.243 g (46%) and BET surface area measurement was 1302 m^2/g.

FT-IR: 3438, 3022, 2966, 2924, 1637, 1602, 1560, 1539, 1510, 1496, 1447, 1152, 1082, 983, 900, 828, 702, 547, 463 cm^{-1}.

Copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside. Polymer 2.

A solution containing styrene (0.25 g, 0.2400 mmol), divinylbenzene (3.00 g, 23.00 mmol), 50 mL benzene, AIBN (0.100 g, 0.7343 mmol) and monomer **3** (0.125 g, 0.2179 mmol) was prepared. The temperature was gradually brought to 80 °C. The weight of the macroporous material was 3.004 g (89%). BET surface area was 528 m^2/g.

FT-IR: 3036, 2910, 1736, 1693, 1631, 1602, 1489, 1455, 1335, 1166, 1103, 990, 900, 835, 786, 702, 561, 463 cm^{-1}.

Copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside. Polymer 3.

A solution was prepared containing styrene (2.714 g, 26.09 mmol), divinylbenzene (3.00 g, 23.00 mmol), 50 mL benzene and monomer **3** (0.125 g, 0.2179 mmol). The temperature was gradually brought to 80 °C. The weight of the macroporous material was 4.028 g (70%). BET surface area analysis gave a surface area of 4 m^2/g.

FT-IR: 3445, 3022, 2924, 2340, 1932, 1869, 1799, 1736, 1630, 1602, 1490, 1447, 1335, 1152, 1089, 1026, 892, 828, 793, 752, 695, 533 cm^{-1}.

Copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside. Polymer 4.

A solution was prepared containing styrene (4.228 g, 40.60mmol), divinylbenzene (3.00 g, 23.00 mmol), 50 mL benzene and monomer **3** (0.125 g, 0.2179 mmol). The temperature was gradually brought to 80 °C. The weight of the macroporous material was 4.380 g (60%). BET analysis gave a surface area of 3 m^2/g.

FT-IR: 3444, 3036, 2917, 1925, 1869, 1736, 1702, 1510, 1482, 1447, 1370, 1335, 1180, 1082, 1025, 885, 825, 793, 702, 547 cm^{-1}.

Copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside. Polymer 5.

A solution was prepared containing styrene (0.621 g, 0.5964 mmol), divinylbenzene (7.26 g, 55.76 mmol), 50 mL benzene, AIBN (0.100 g, 0.7343 mmol) and the monomer **3** (1.85 g, 0.323 mmol). The weight of the macroporous material was 5.52 g (57%). BET analysis gave a value of 85 m^2/g.

FT-IR: 3437, 3093, 3029, 2917, 1736, 1630, 1595, 1529, 1447, 1377, 1342, 1243, 1124, 982, 948, 906, 835, 794, 751, 702, 526, 477 cm^{-1}.

Blank copolymer of styrene and divinylbenzene. Polymer 6. Method B.

A solution containing styrene (0.245 g, 2.352 mmol), divinylbenzene (2.451 g, 18.80 mmol), AIBN (0.050 g, 0.300 mmol) and 2.5 mL of toluene was placed in a medium-walled glasstube which had a constricted neck for sealing. The tubing was then placed in an oil bath where it was incubated at 50 °C for 12 hours and then at 100 °C for 36 hours. The tube was cooled and broken open and the yellow crumbly polymer was ground up with a mortar and pestle. A total of 2.29 g (62%) of product was recovered and BET analysis gave a value of 537 m^2/g.

FT-IR: 3437, 3022, 2917, 2924, 2347, 1932, 1862, 1792, 1630, 1603, 1518, 1483, 1447, 1363, 1125, 1166, 1096, 1053, 1018, 893, 828, 794, 695, 561, 463 cm^{-1}.

Copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside. Polymer 7.

A solution was prepared containing divinylbenzene (3.00 g, 23.00 mmol), styrene (2.714 g, 26.09 mmol), 50 mL toluene, AIBN (0.100 g, 0.7343 mmol) and monomer **3** (0.125 g, 0.2179 mmol). The temperature was gradually brought to 90 °C. The weight of the macroporous material was 4.028 g (78%). BET surface area measurements gave a value of 1 m^2/g.

FT-IR: 3452, 3022, 2889, 1940, 1870, 1800, 1735, 1602, 1490, 1447, 1335, 1140, 1025, 900, 835, 794, 752, 702, 540 cm^{-1}.

Copolymer 4-nitrophenyl 2,3,4,5-tetra-O-methacryloyl-α-D-glucopyranoside. Polymer 8.

A solution was prepared containing divinylbenzene (10.00 g, 76.80 mmol), 50 mL toluene, AIBN (0.100 g, 0.7343 mmol) and monomer **3** (0.125 g, 0.2179 mmol). The temperature was gradually brought to 90 °C. The weight of the macroporous material was 3.24g (72%). BET surface area measurements gave a value of 487 m^2/g.

FT-IR: 3482, 3019, 2956, 2928, 2736, 1736, 1625, 1598, 1535, 1486, 1452, 1346, 1241, 1163, 1100, 1044, 988, 897, 834, 792, 717 cm^{-1}.

Copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside.

Polymer 9. Method B.

A solution containing divinylbenzene (5.00 g, 38.40mmol), AIBN (0.050 g, 0.300 mmol), monomer **3** (0.125 g, 0.2179 mmol) and 2.5 mL of toluene was placed in a medium-walled glasstube which had a constricted neck for sealing. The tube was placed in an oil bath where it was incubated at 50 °C for 12 hours and then at 100 °C for 36 hours. 4.442 g (79%) product was recovered and BET analysis gave a value of 739 m^2/g. **FT-IR:** 3437, 3022, 2924, 1736, 1637, 1603, 1560, 1483, 1447, 1363, 1125, 1166, 1096, 1053, 1018, 893, 828, 794, 695, cm^{-1}.

Copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside.

Polymer 10.

A solution was prepared containing divinylbenzene (5.00 g, 38.40 mmol), 50 mL toluene, AIBN (0.050 g, 0.300 mmol) and monomer **3** (0.750 g, 0.13076 mmol). The temperature was gradually brought to 90 °C. The weight of the macroporous material was 6.137 g (89%). BET surface area measurements gave a value of 712 m^2/g.

FT-IR: 3465, 3029, 2980, 2924, 2333, 1736, 1630, 1602, 1525, 1489, 1447, 1342, 1243, 1173, 1103, 1032, 984, 900, 835, 793, 702, 568 cm^{-1}.

Blank copolymer of styrene and divinylbenzene. Polymer 11.

A solution was prepared containing divinylbenzene (2.45 g, 23 mmol), 50 mL tetrahydrofuran (THF) and AIBN (0.050 g, 0.300 mmol). The temperature was gradually brought to 60 °C. The weight of the macroporous material was 1.532 g (56%). BET surface area was found to be 421 m^2/g.

FT-IR: 3438, 3029, 2966, 2924, 1637, 1602, 1560, 1539, 1510, 1496, 1447, 1152, 1082, 983, 900, 828, 702, 547, 463 cm^{-1}.

Copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside. Polymer 12.

A solution was prepared containing styrene (1.343 g, 0.1289 mmol), divinylbenzene (3.00 g, 2.304 mmol), 50 mL THF, AIBN (0.100 g, 0.7343 mmol) and the monomer **3** (0.125 g, 0.2179 mmol). The temperature was gradually brought to 60 °C. The weight of the macroporous material was 2.89 g (65%). BET surface area was found to be was 1365 m^2/g.

FT-IR: 3445, 3029, 2931, 1939, 1855, 1736, 1630, 1602, 1510, 1489, 1447, 1342, 1260, 1166, 1096, 1018, 900, 786, 702, 547 cm^{-1}.

Copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside. Polymer 13.

Starch (0.500 g) was dissolved in 50 mL of water, then poured into the 3-neck flask. A solution was prepared containing styrene (0.322 g, 0.312 mmol), divinylbenzene (3.175 g, 24.29 mmol), 50 mL THF, AIBN (0.012 g, 0.0881 mmol) and monomer **3** (0.512 g, 0.0893 mmol). The weight of the macroporous material was 1.763 g (44%). BET gave a surface area of 0.2 m^2/g.

FT-IR: 3445, 3022, 2959, 2924, 2348, 1736, 1630, 1595, 1525, 1489, 1440, 1335, 1236, 1160, 1096, 1033, 906, 835, 793, 702, 470 cm^{-1}.

Copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside. Polymer 14.

A solution was prepared containing styrene divinylbenzene (3.00 g, 23.00 mmol), 50 mL THF, AIBN (0.100 g, 0,7343 mmol) and monomer **3** (0.704 g, 0.1228 mmol). The temperature was gradually brought to 60 °C. The weight of the macroporous material was 4.028g (82%). BET analysis gave a surface area of 1045 m^2/g.

FT-IR: 3465, 3029, 2980, 2924, 2333, 1736, 1630, 1602, 1525, 1489, 1447, 1342, 1243, 1173, 1103, 1032, 984, 900, 835, 793, 702, 568 cm^{-1}.

Blank copolymer of styrene and divinylbenzene. Polymer 15.

A solution was prepared containing divinylbenzene (3.00 g, 23.00 mmol), 50 mL of acetonitrile and AIBN (0.100 g, 0.7343 mmol). The temperature was gradually brought to 75 °C. The weight of the macroporous material was 2.362 g (79%). BET surface area measurement gave a value of 114 m^2/g.

FT-IR: 3438, 3022, 2966, 2924, 1638, 1595, 1510, 1490, 1450, 1370, 1237, 1160, 1054, 984, 900, 828, 786, 709, 562 cm^{-1}.

Blank copolymer of styrene and divinylbenzene. Polymer 16 Method B.

A solution containing styrene (0.245 g, 2.352 mmol), divinylbenzene (2.451 g, 18.8 mmol), AIBN (0.050 g, 0.300mmol) and 2.5 mL of acetonitrile was placed in a medium-walled glasstube which had a constricted neck for sealing. The tube was placed in an oil bath where it was incubated at 50 °C for 12 hours and then at 100 °C for 36 hours. Mass of the product was 1.894 g (70%) and BET surface measurements gave a value of 97 m^2/g.

FT-IR: 3437, 3022, 2917, 2924, 2347, 1932, 1862, 1792, 1630, 1603, 1518, 1483, 1447, 1363, 1125, 1166, 1096, 1053, 1018, 893, 828, 794, 695, 561, 463 cm^{-1}.

Blank copolymer of styrene and divinylbenzene. Polymer 17.

A solution was prepared containing divinylbenzene (3.00 g, 23.00 mmol), 50 mL of pyridine and AIBN (0.100 g, 0.7343 mmol). The temperature was gradually brought to 80 °C. The weight of the macroporous material was 2.482 g (83%). BET surface area measurement gave a value of 39 m^2/g.

FT-IR: 3438, 3029, 2966, 2924, 1637, 1602, 1560, 1539, 1510, 1496, 1447, 1152, 1082, 983, 900, 828, 702, 547, 463 cm^{-1}.

Copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside. Polymer 18.

A solution was prepared containing styrene (1.343 g, 0.1289 mmol), divinylbenzene (3.00 g, 23.00 mmol), 50 mL pyridine, AIBN (0.100 g, 0.7343 mmol) and monomer **3** (0.125 g, 0.2179 mmol). The temperature was gradually brought to 80 °C. The weight of the macroporous material was 3.24 g (73%). BET surface area measurement gave a value of 145 m^2/g.

FT-IR: 3445, 3022, 2931, 2853, 1736, 1630, 1602, 1518, 1489, 1440, 1370, 1166, 1075, 900, 835, 793, 702 cm^{-1}.

Hydrolysis of the Template Molecule

A 0.055 M molar solution of KOH was prepared by dissolving 3.10 g KOH in water and diluting to 1L. To a 250 mL-round-bottomed flask containing 100 mL KOH of the solution was added to 2.00 g of the polymer. The suspension was stirred at room temperature for 24 hrs. After stirring for about 1 hour a yellow colour change was noticed. After refluxing for 24 hours, the polymer was filtered and washed with 2 x 20 mL of acetone, 2 x 30 mL of water and 20mL of acetone to remove any unreacted material. The polymer was transferred to a Soxhlet extractor for further extraction overnight with acetone and then dried to constant weight under a vacuum at 100 °C. The filtrate was combined and analyzed for the template by TLC (ethyl acetate: petrol ether 5: 1) and UV analysis (methanol). The template molecule had λ_{max} = 300nm and 4-nitrophenoxide ion had λ_{max} = 398 nm.

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SPECTRA

Figure 6 IR Spectrum of blank polydivinylbenzene, Polymer 1

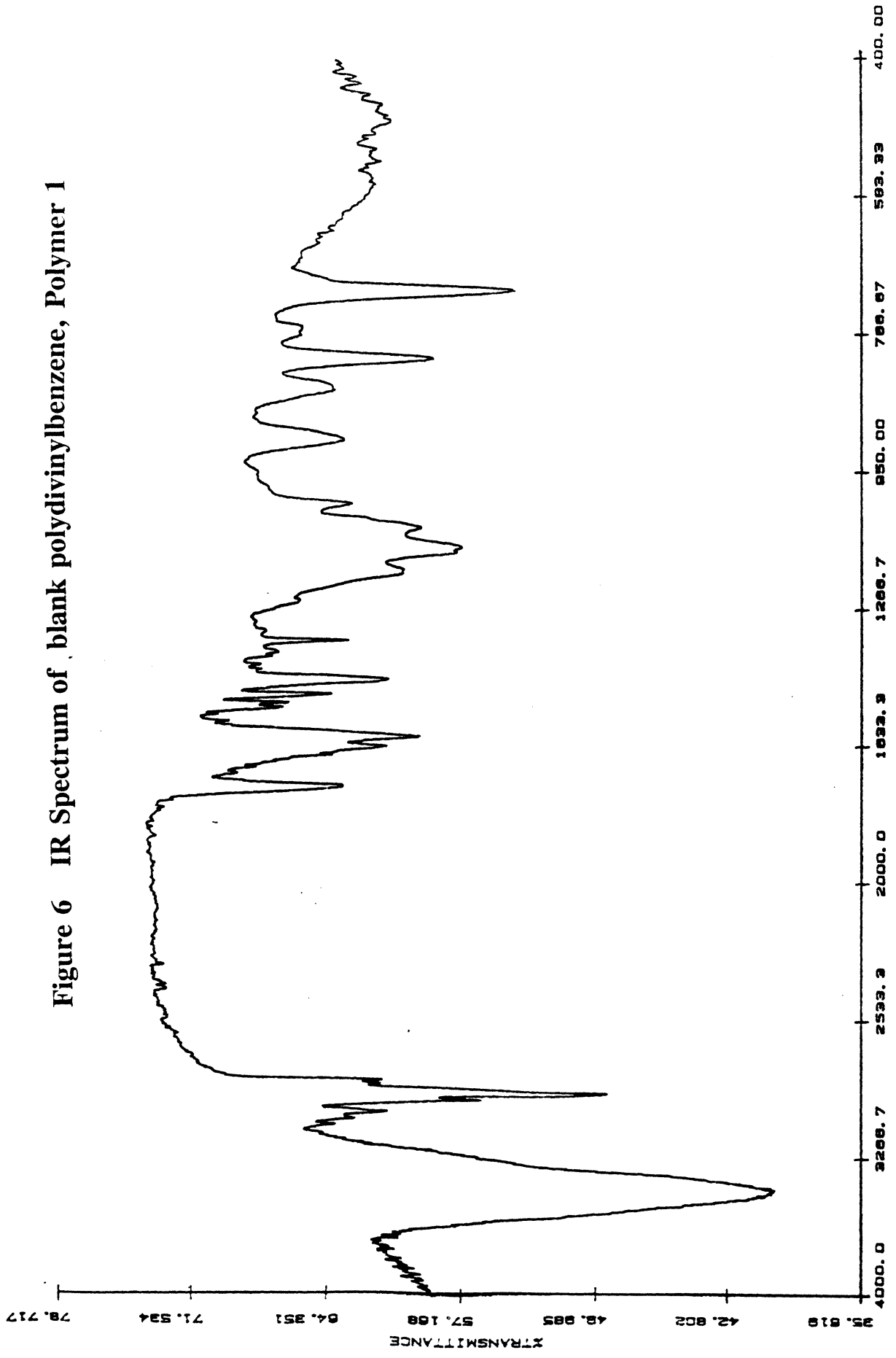


Figure 6 IR Spectrum of blank polydivinylbenzene, Polymer 1

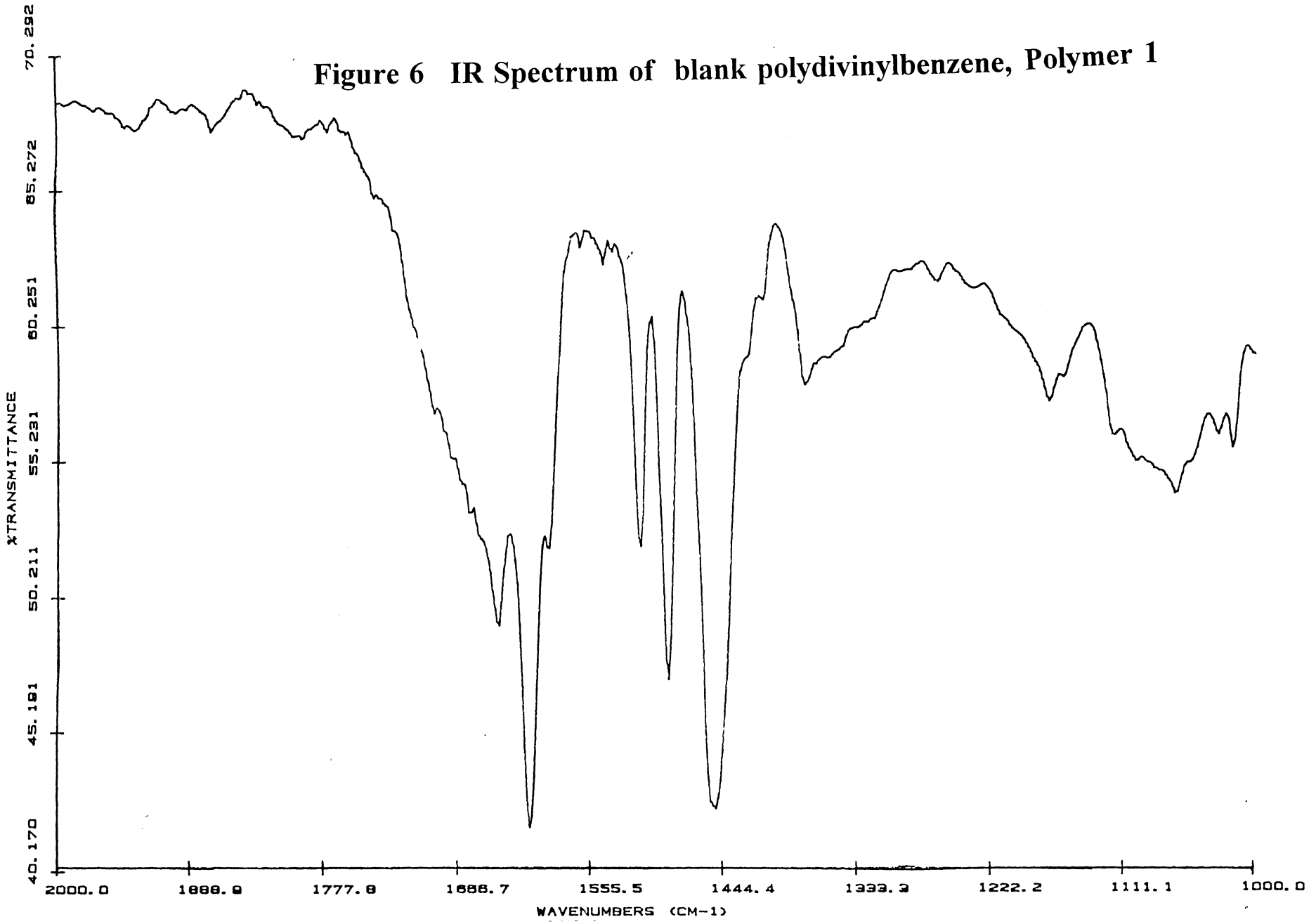


Figure 7 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 2

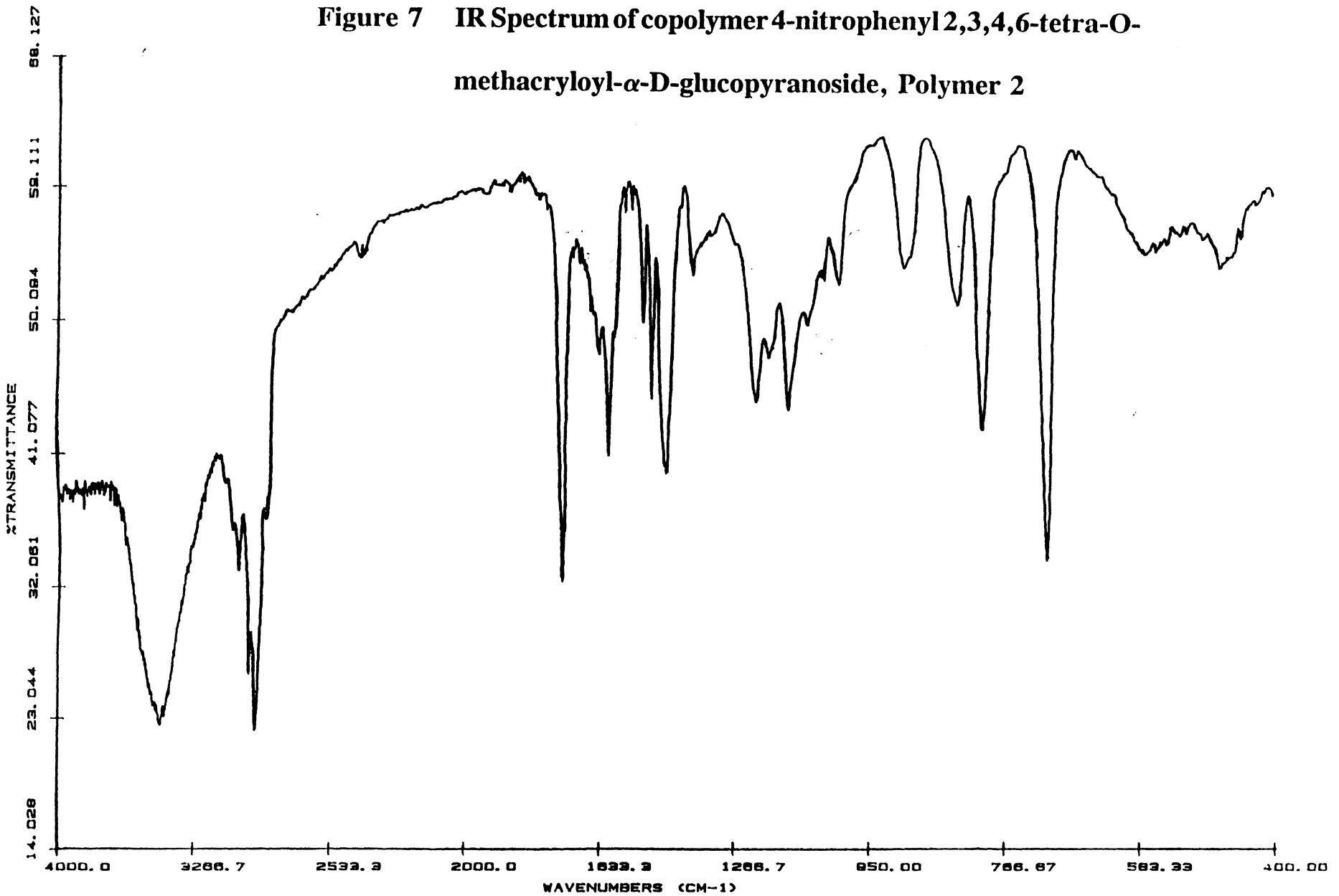


Figure 7 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 2

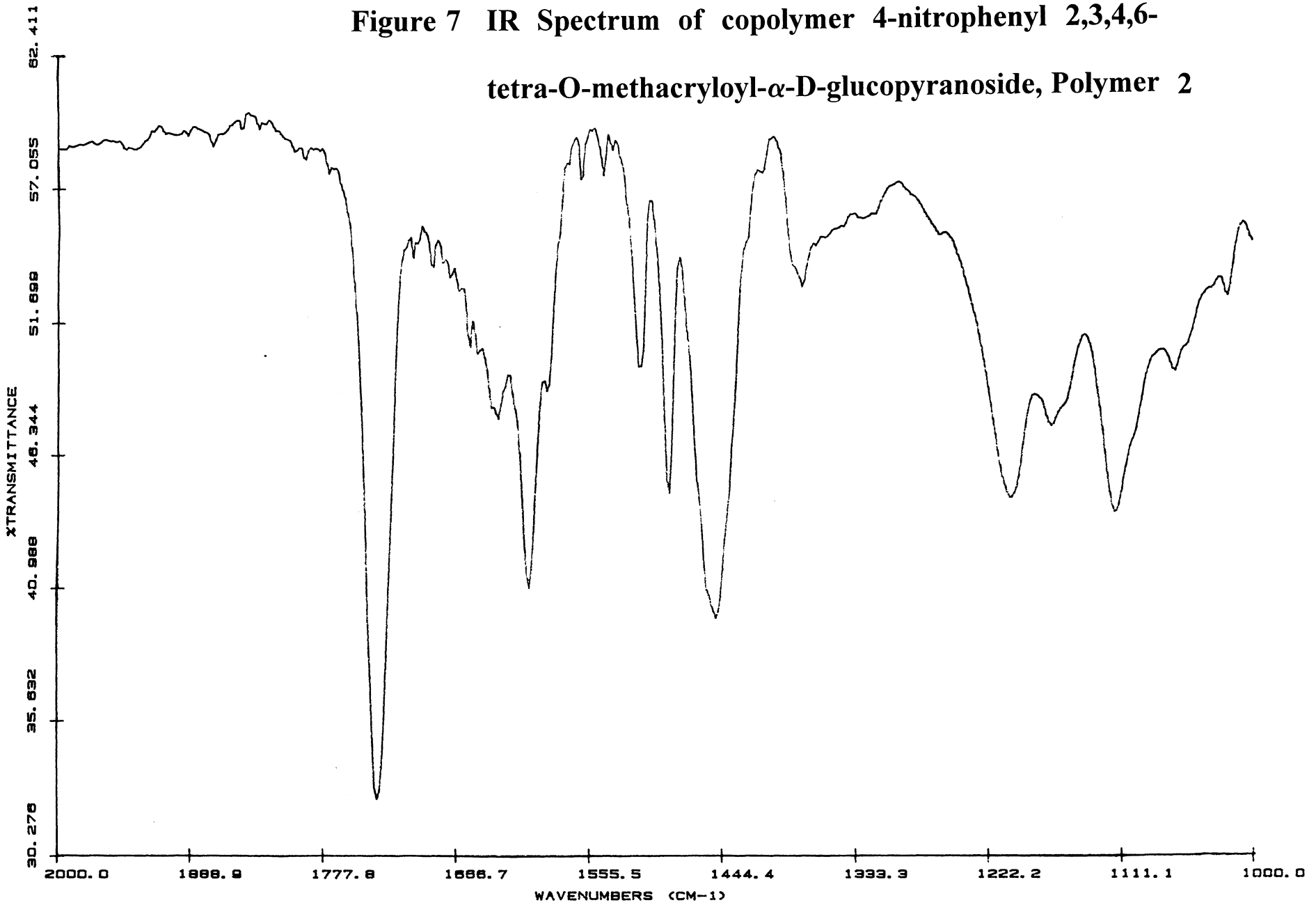


Figure 8 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 3

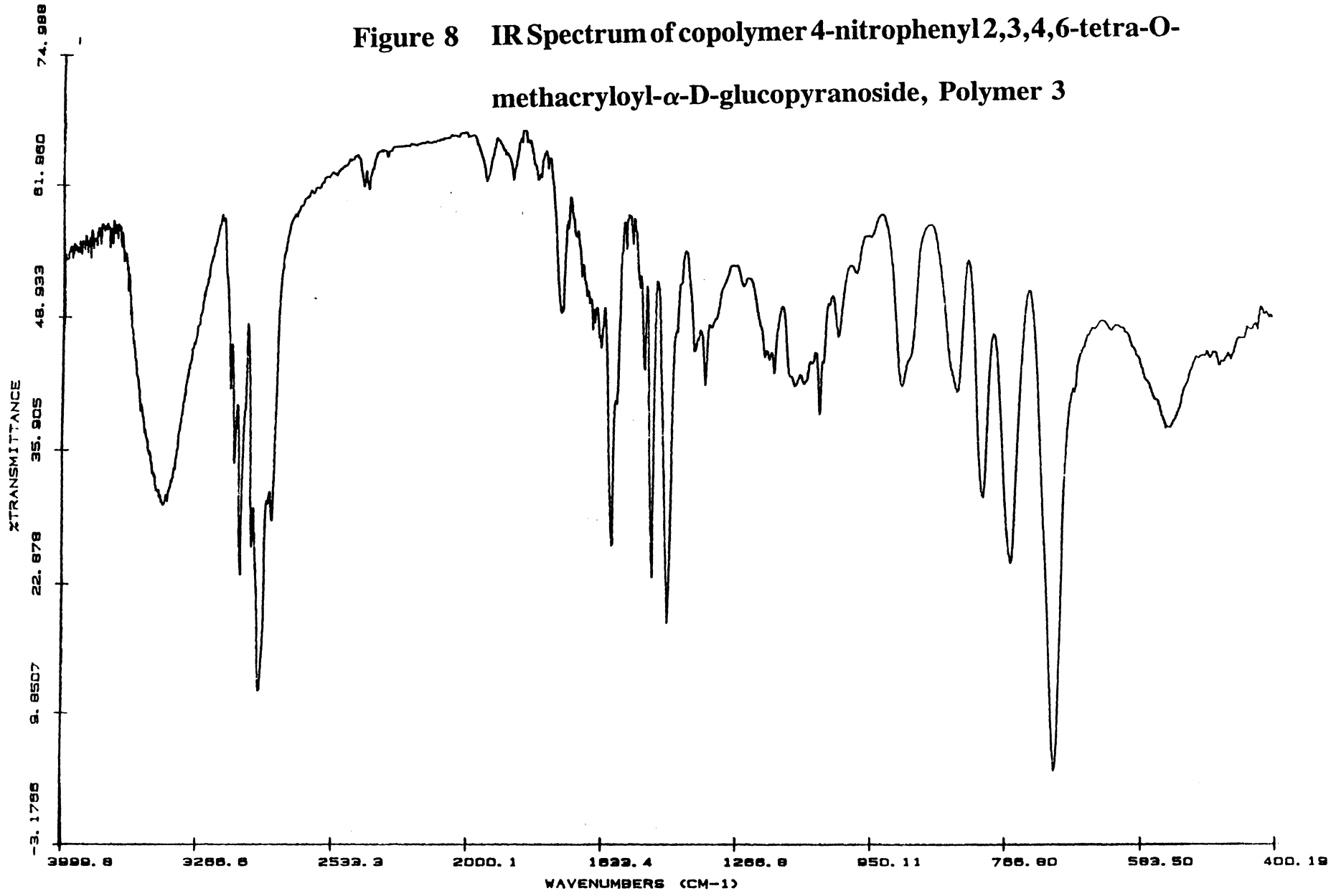


Figure 8 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 3

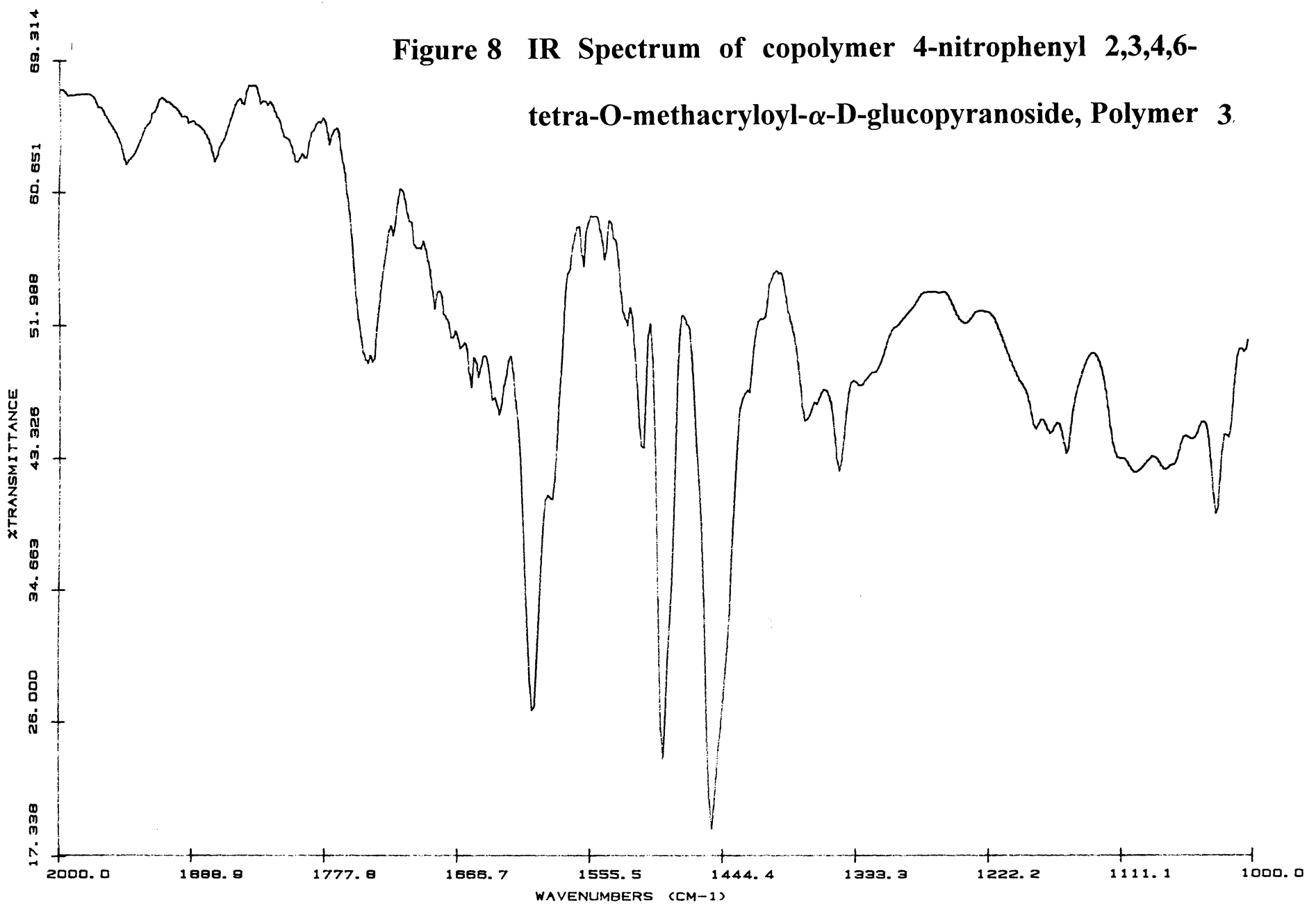


Figure 9 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 4

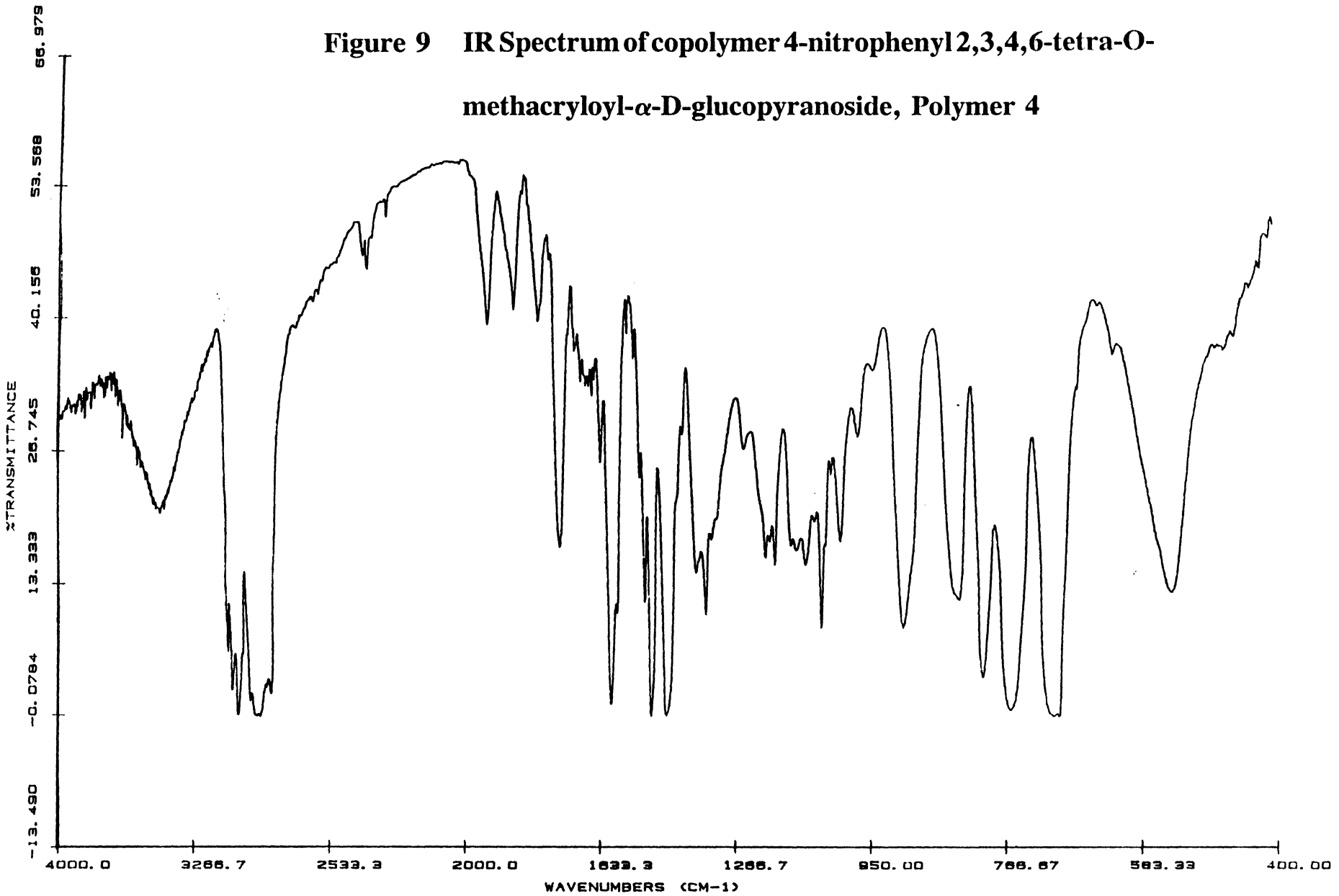


Figure 9 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer *4*

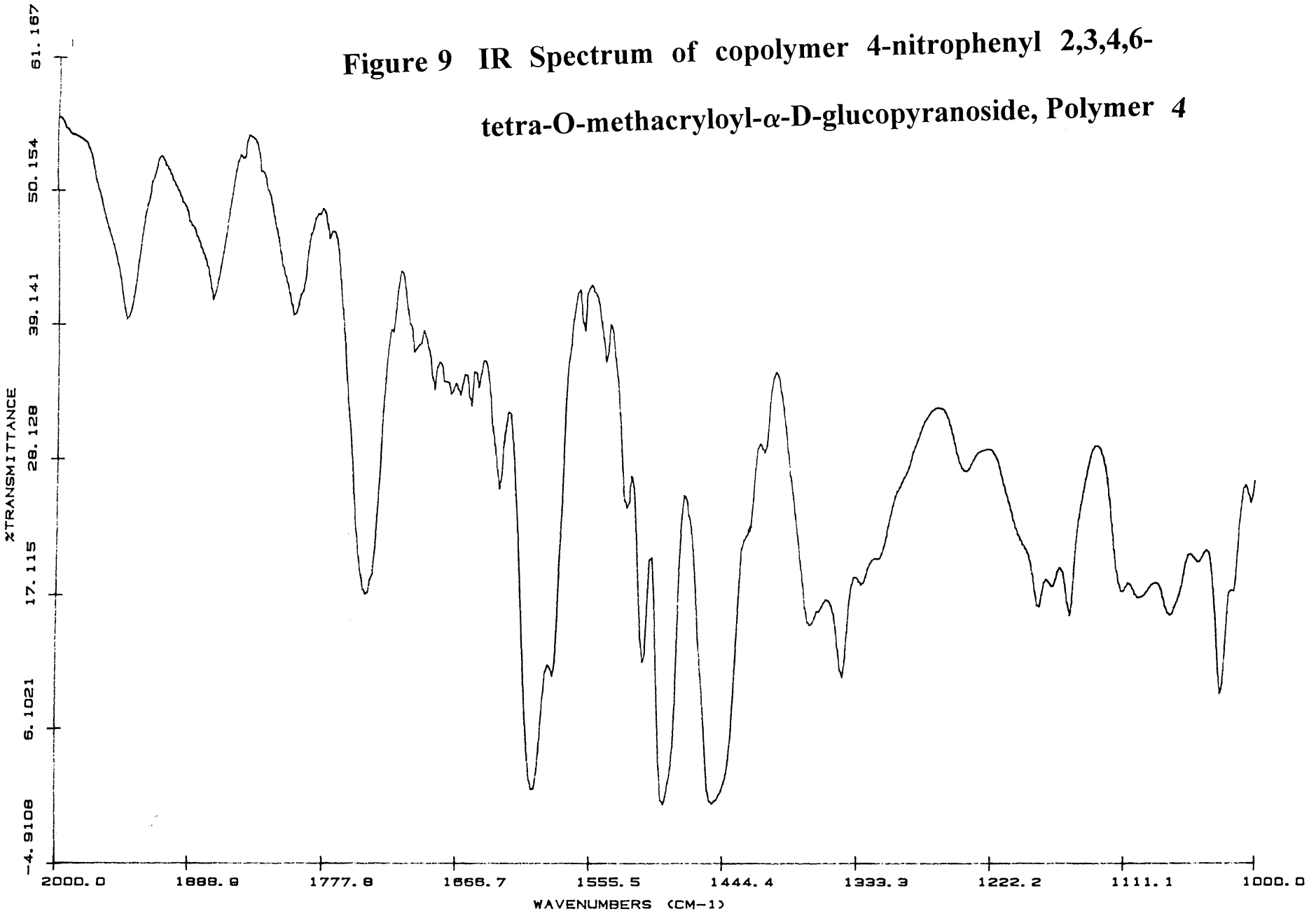


Figure 10 IR Spectrum of copolymer 4-nitrophenyl2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 5

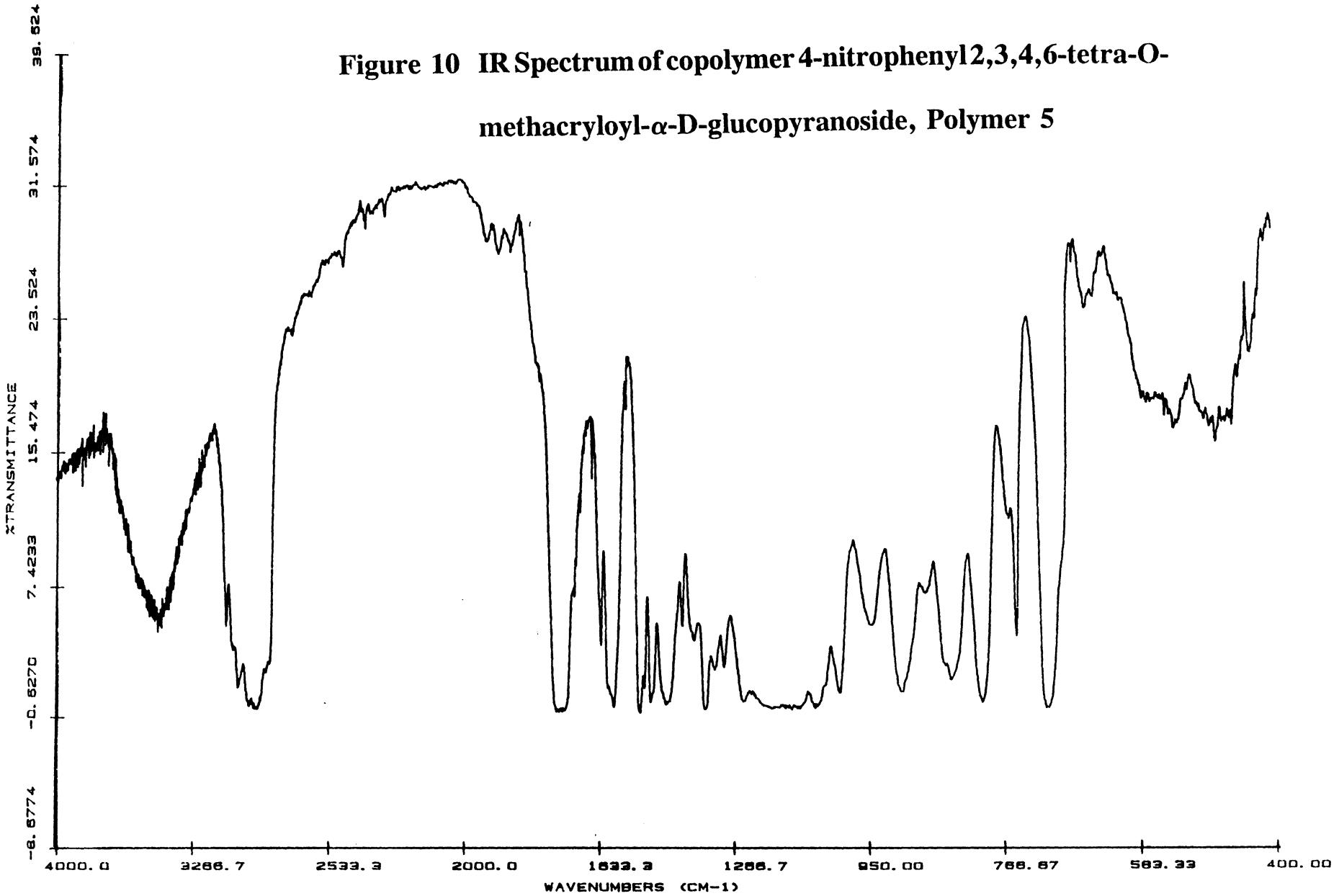


Figure 10 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 5

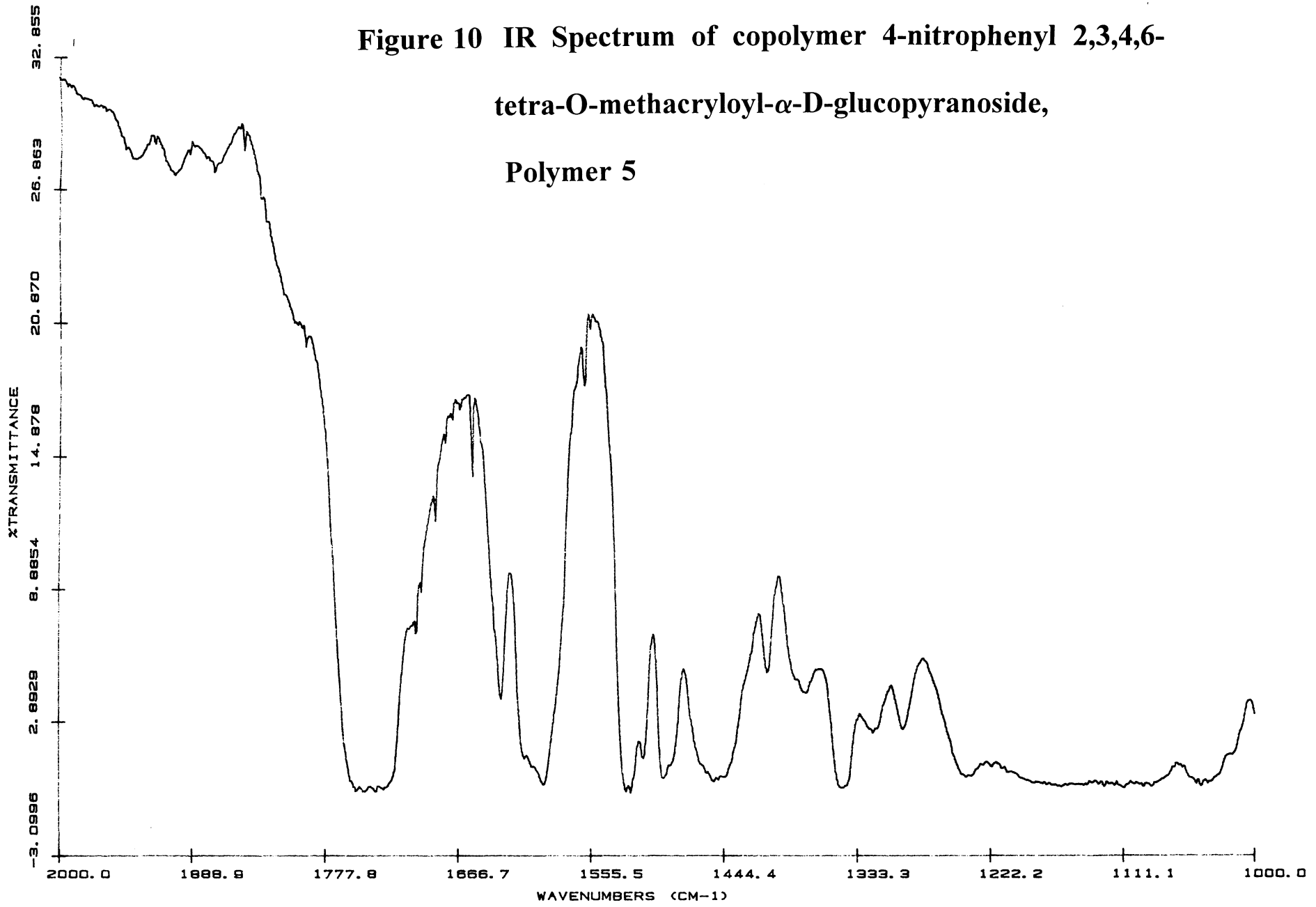


Figure 11 IR Spectrum of blank polydivinylbenzene, Polymer 6

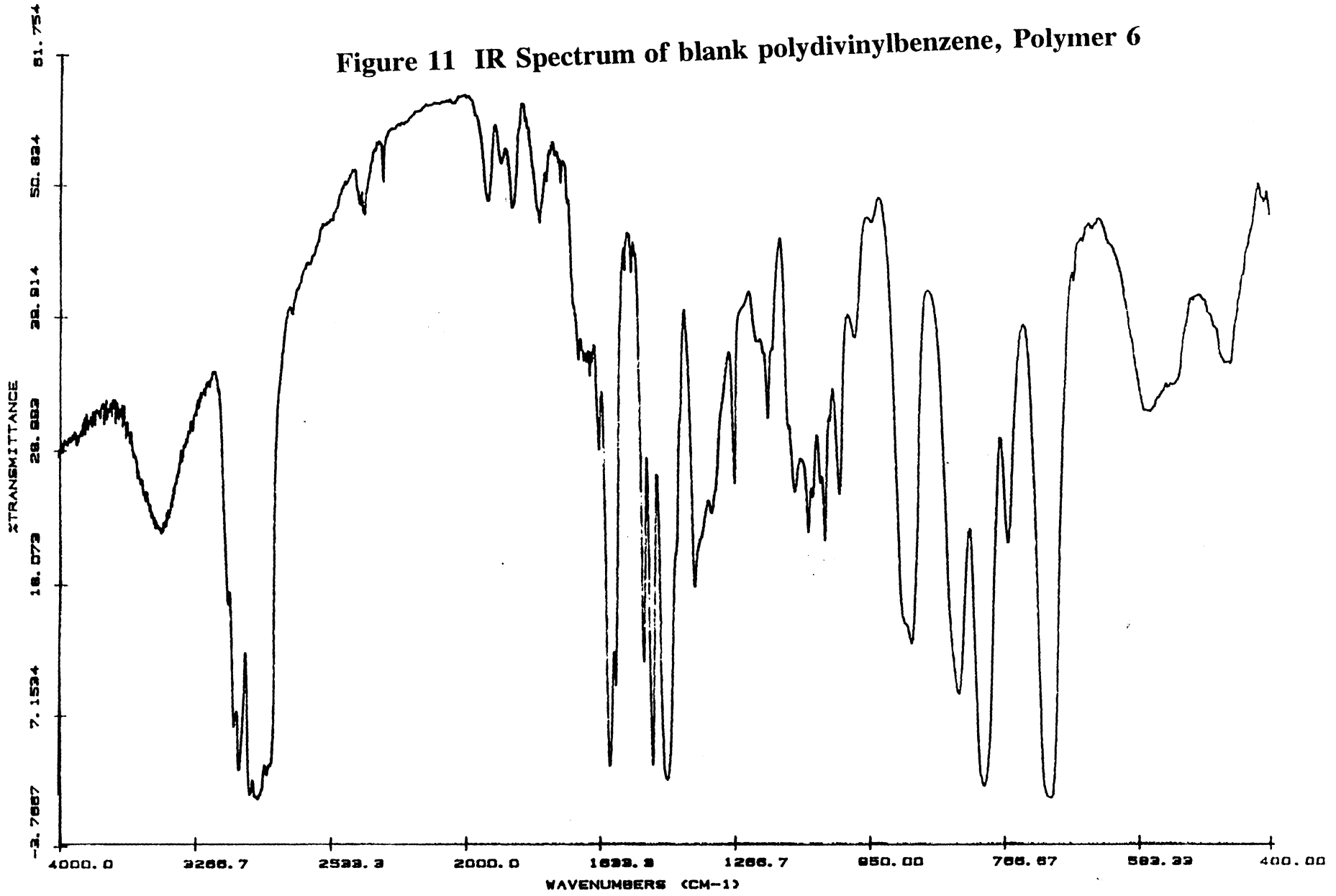


Figure 11 IR Spectrum of blank polydivinylbenzene, Polymer 6

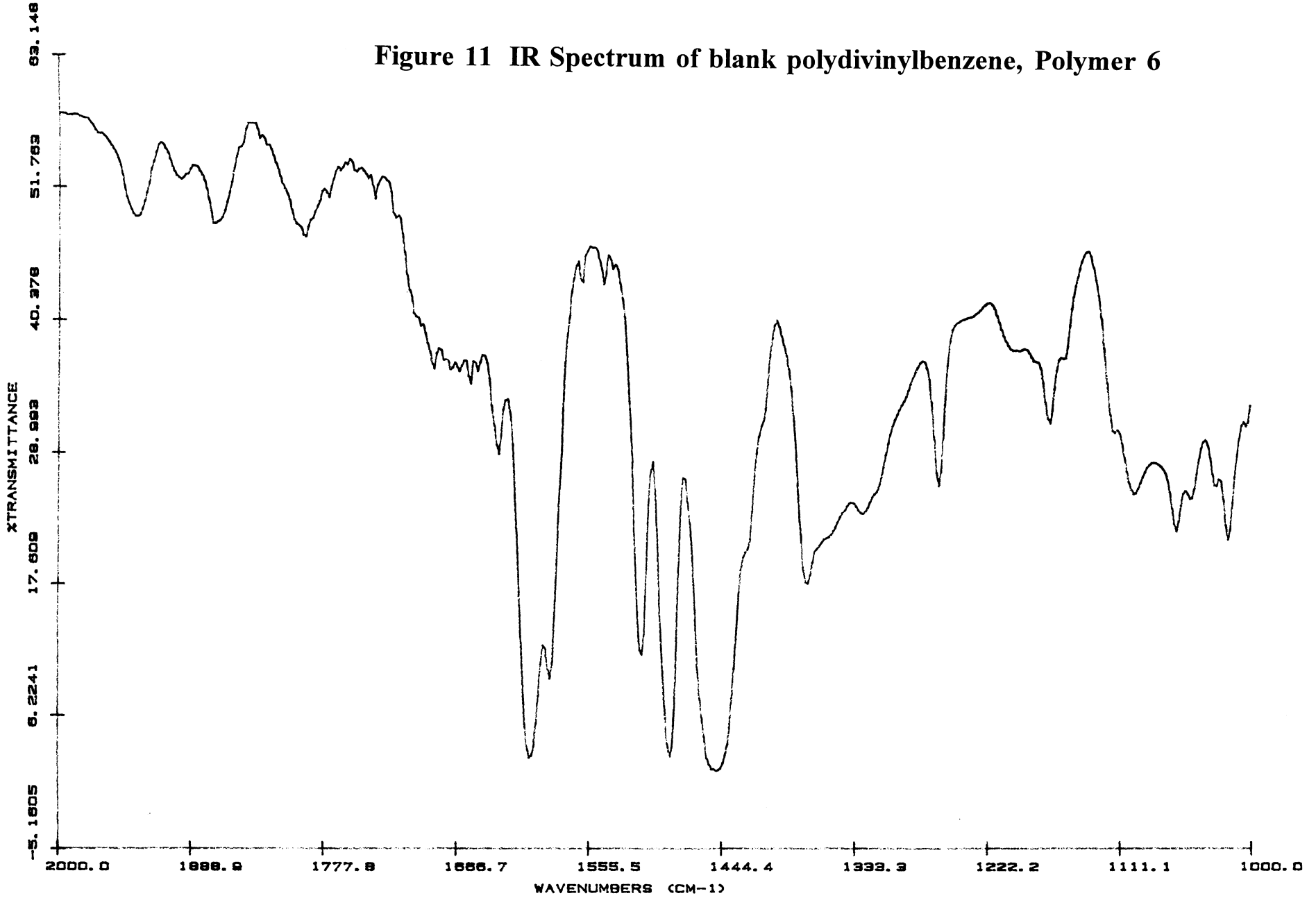


Figure 12 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 7

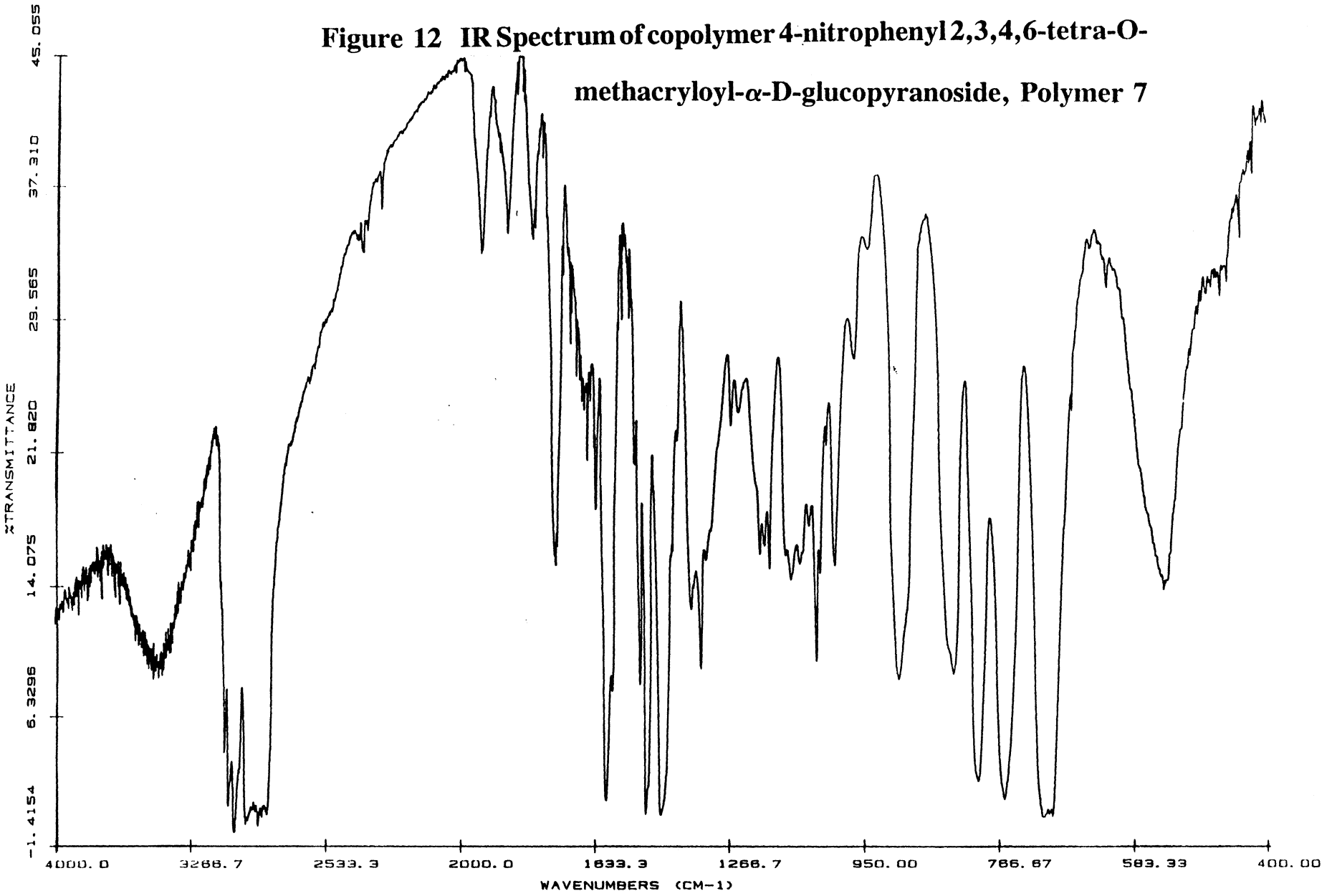


Figure 12 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 7

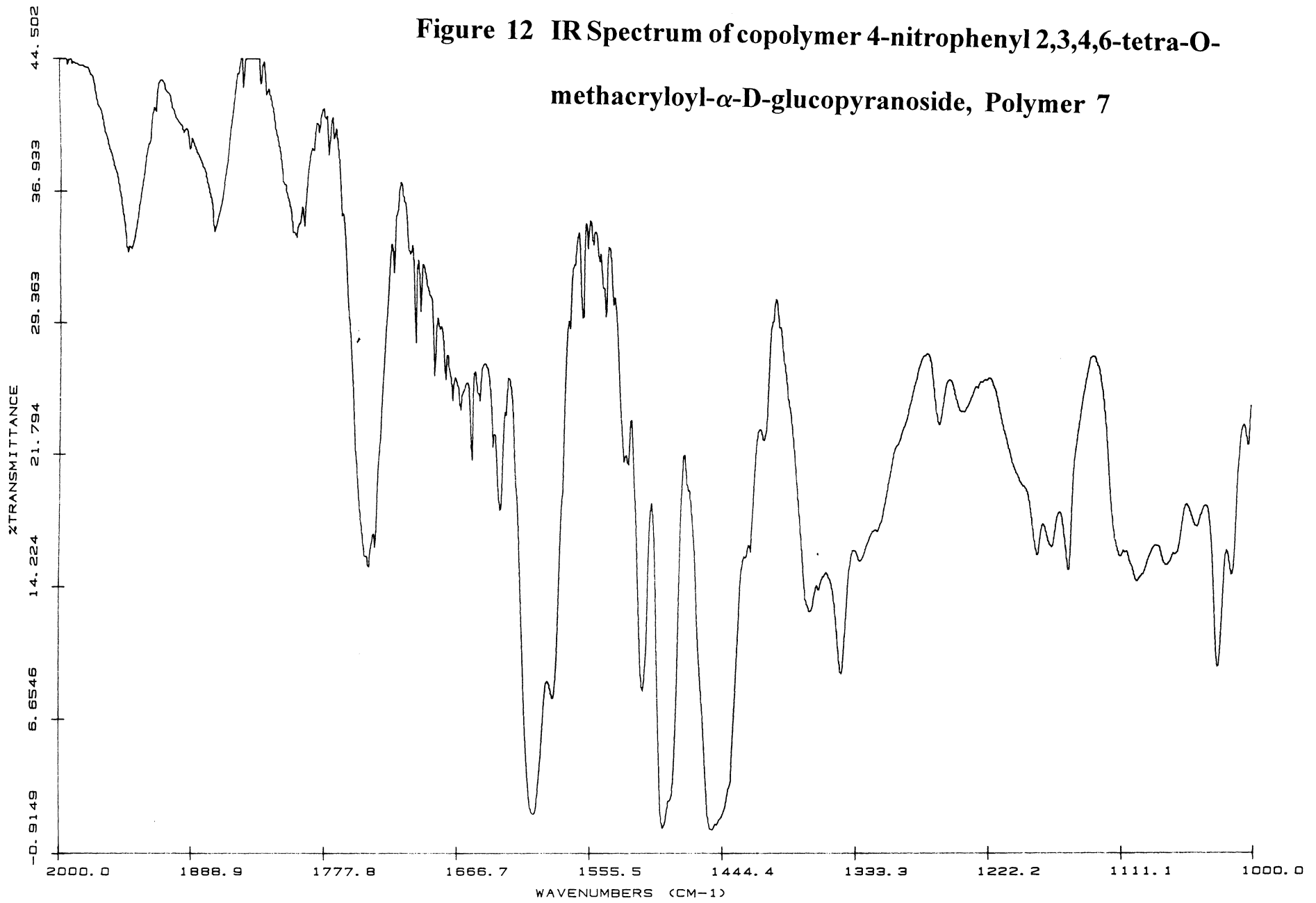


Figure 13 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 8

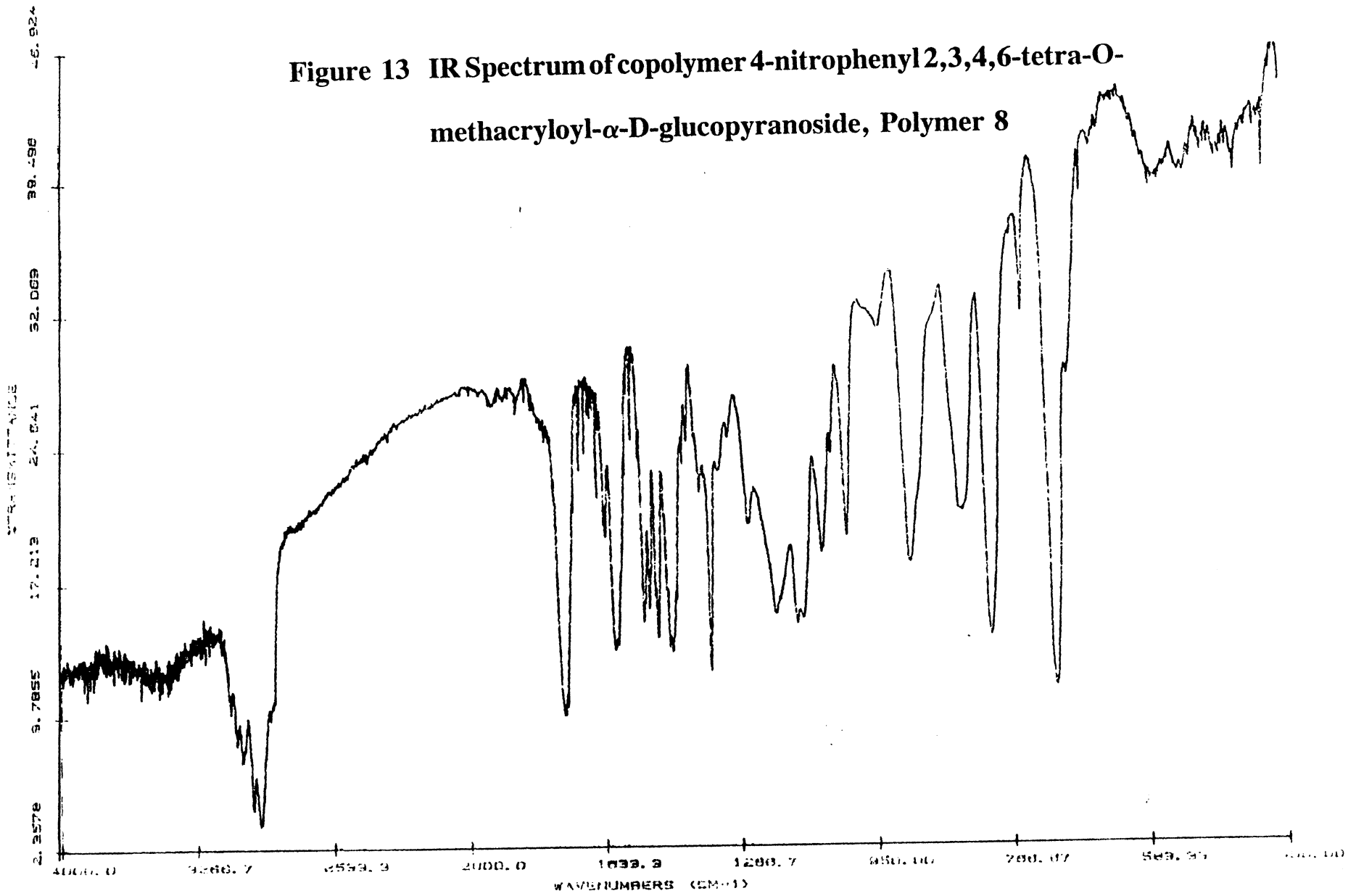


Figure 13 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 8

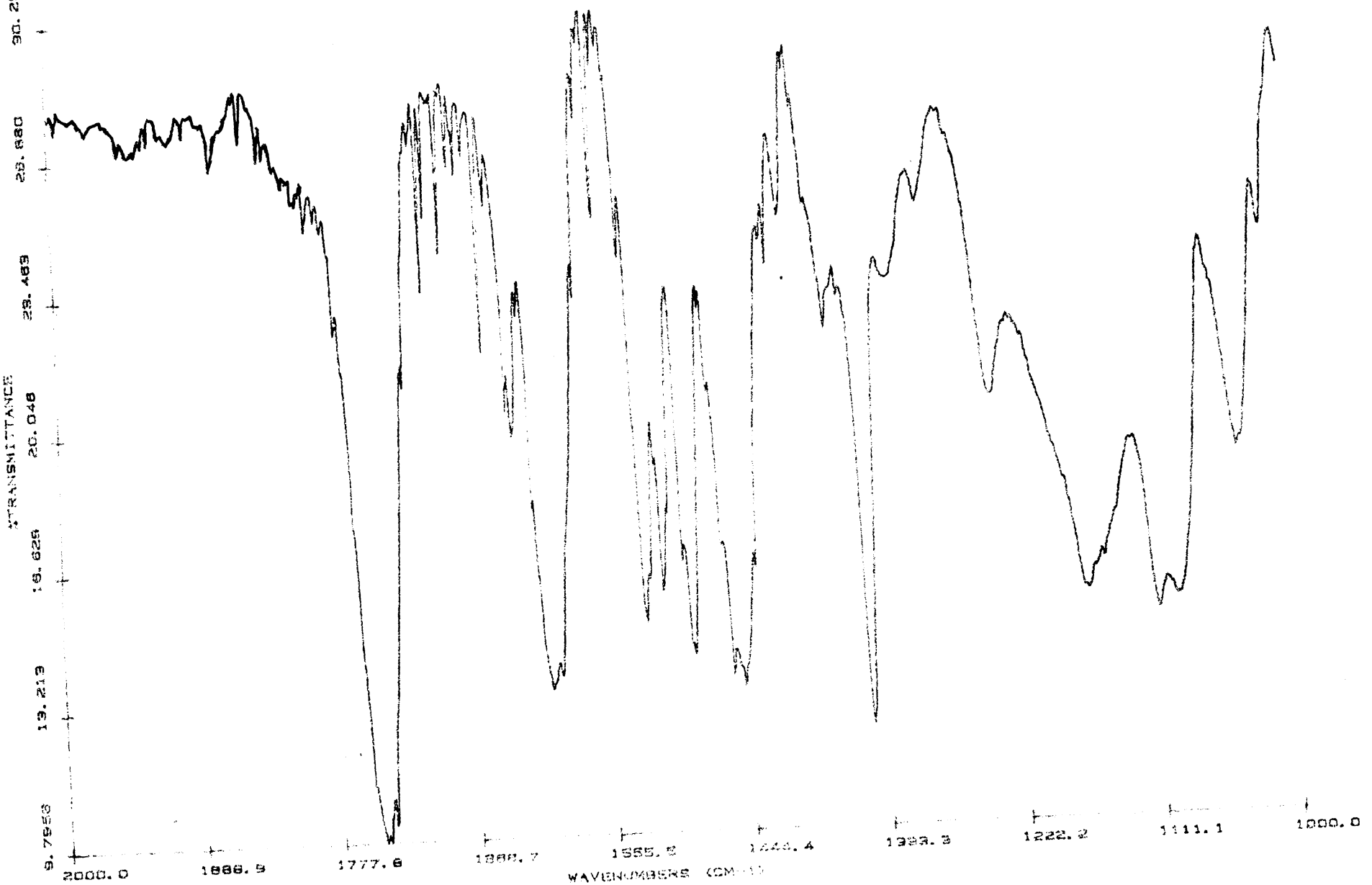


Figure 14 IR Spectrum of copolymer 4-nitrophenyl2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 9

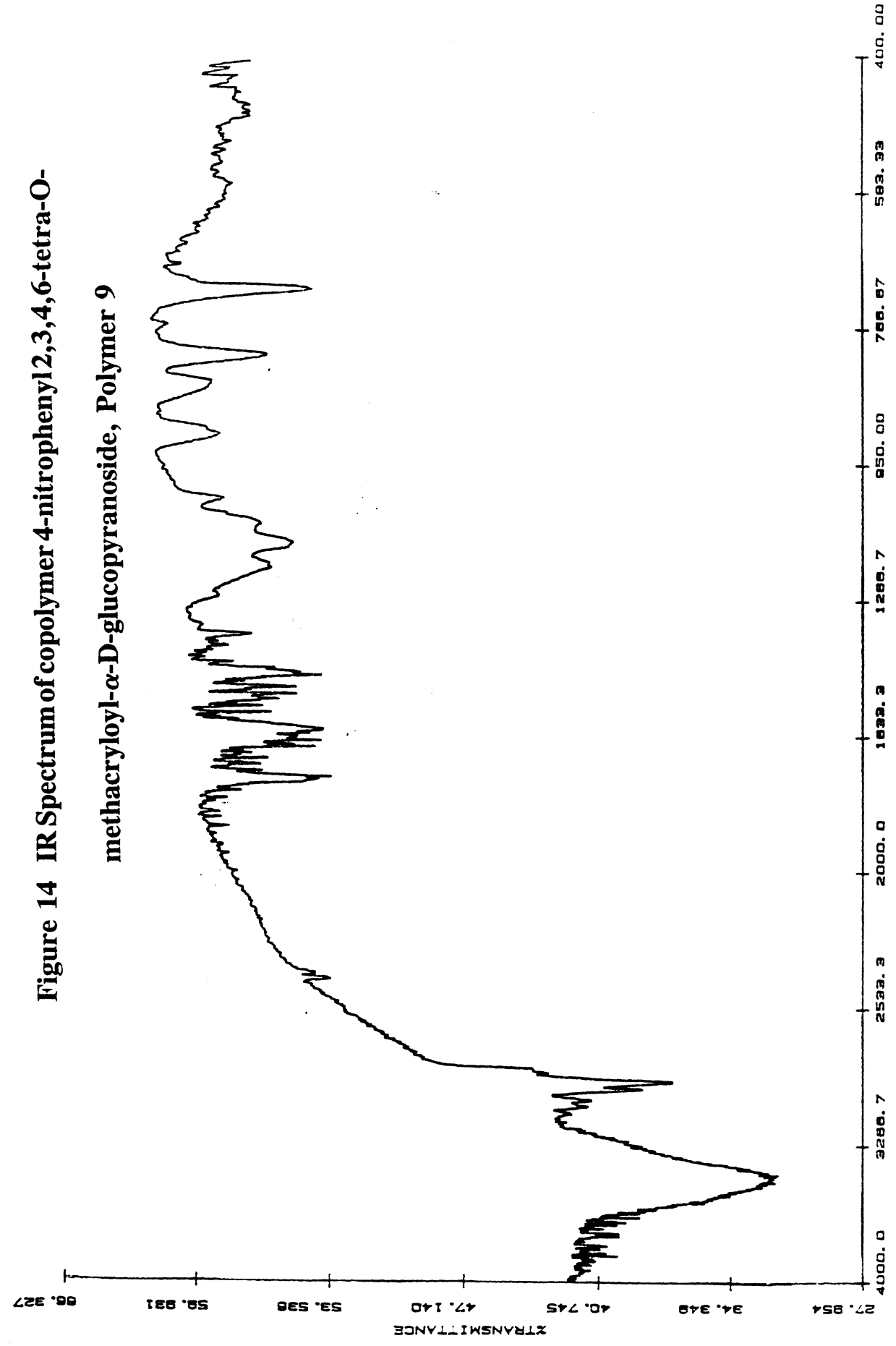


Figure 14 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 9

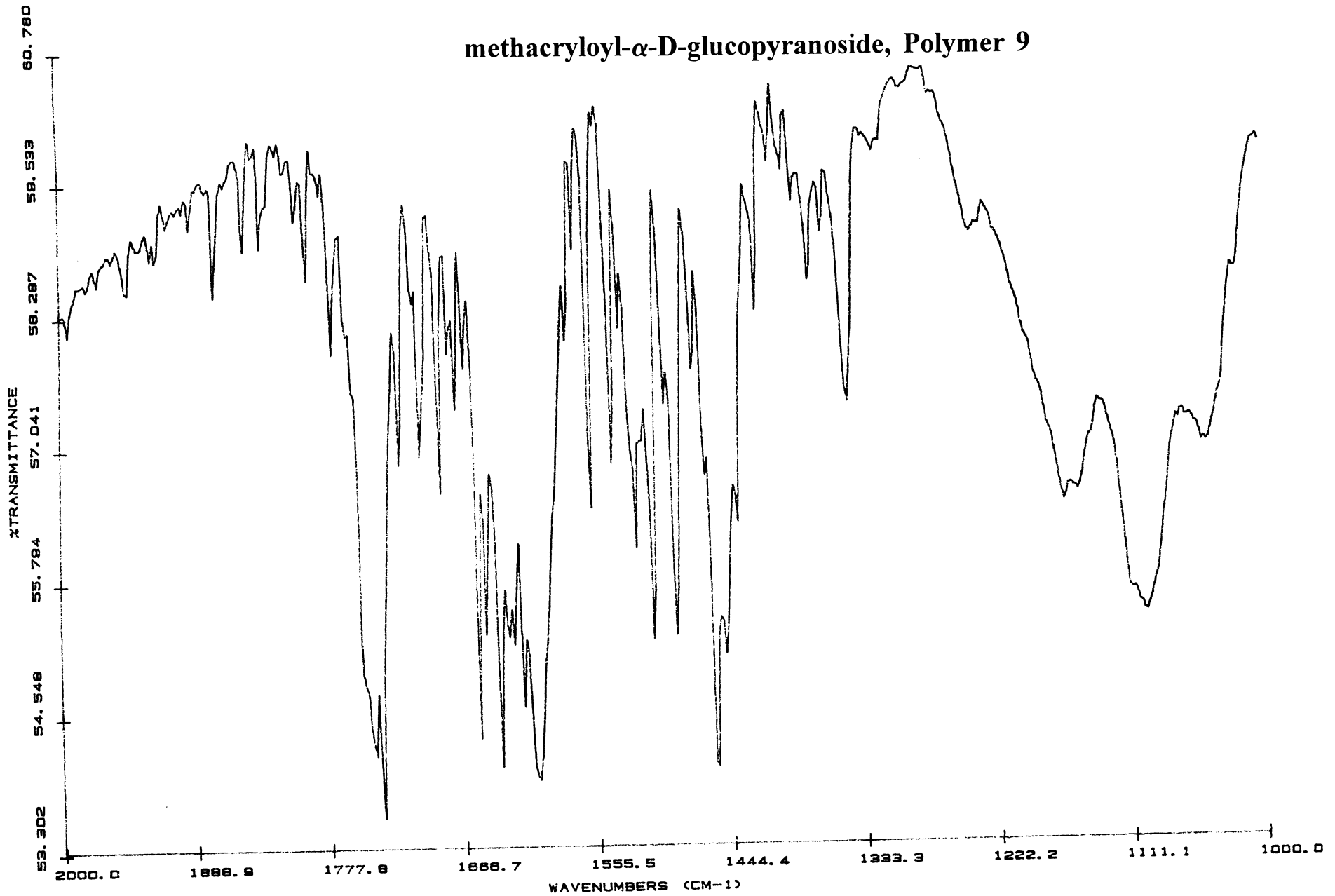


Figure 15 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 10

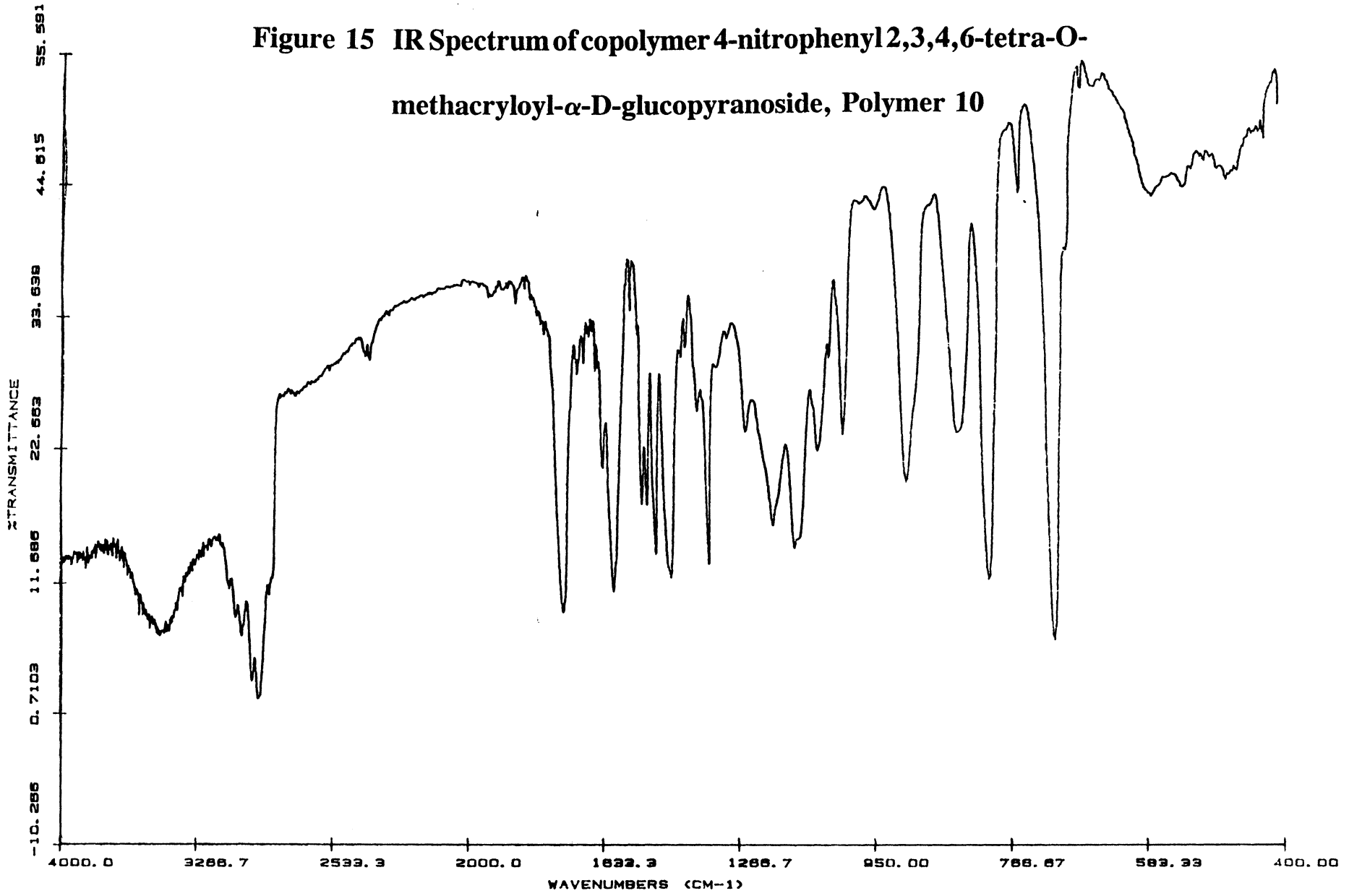


Figure 15 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 10

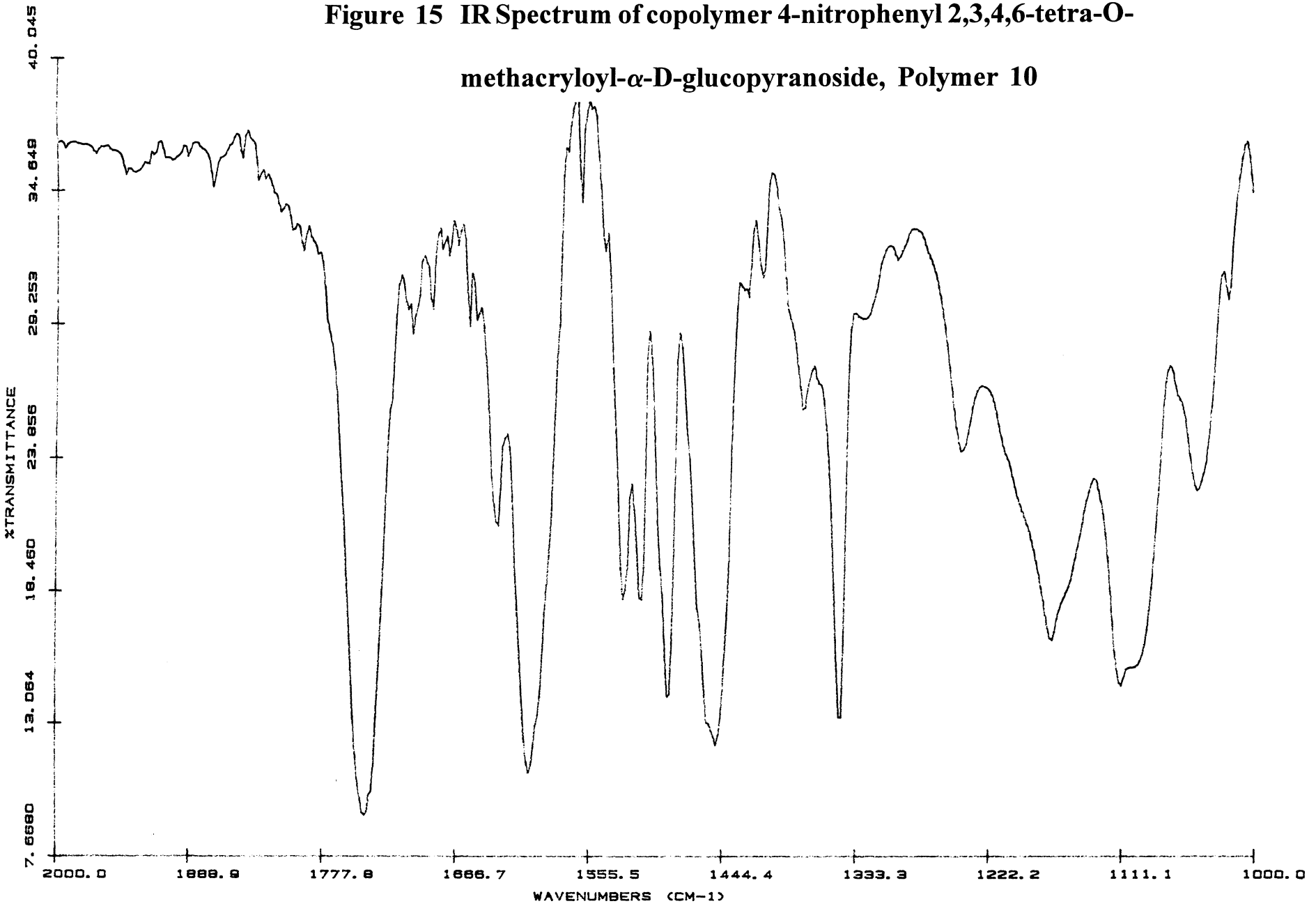


Figure 16 IR Spectrum of blank polydivinylbenzene, Polymer 11

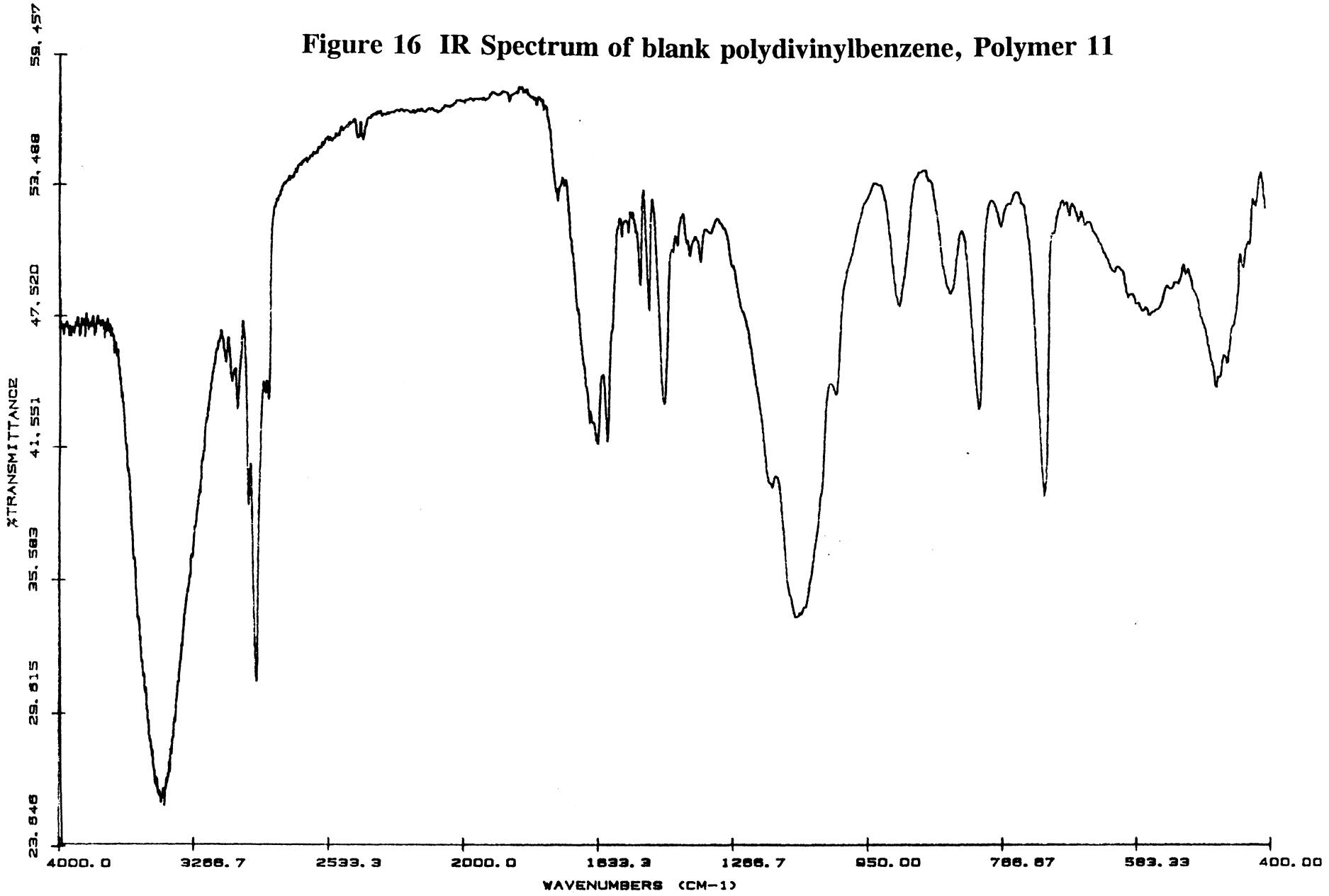


Figure 16 IR Spectrum of blank polydivinylbenzene, Polymer 11

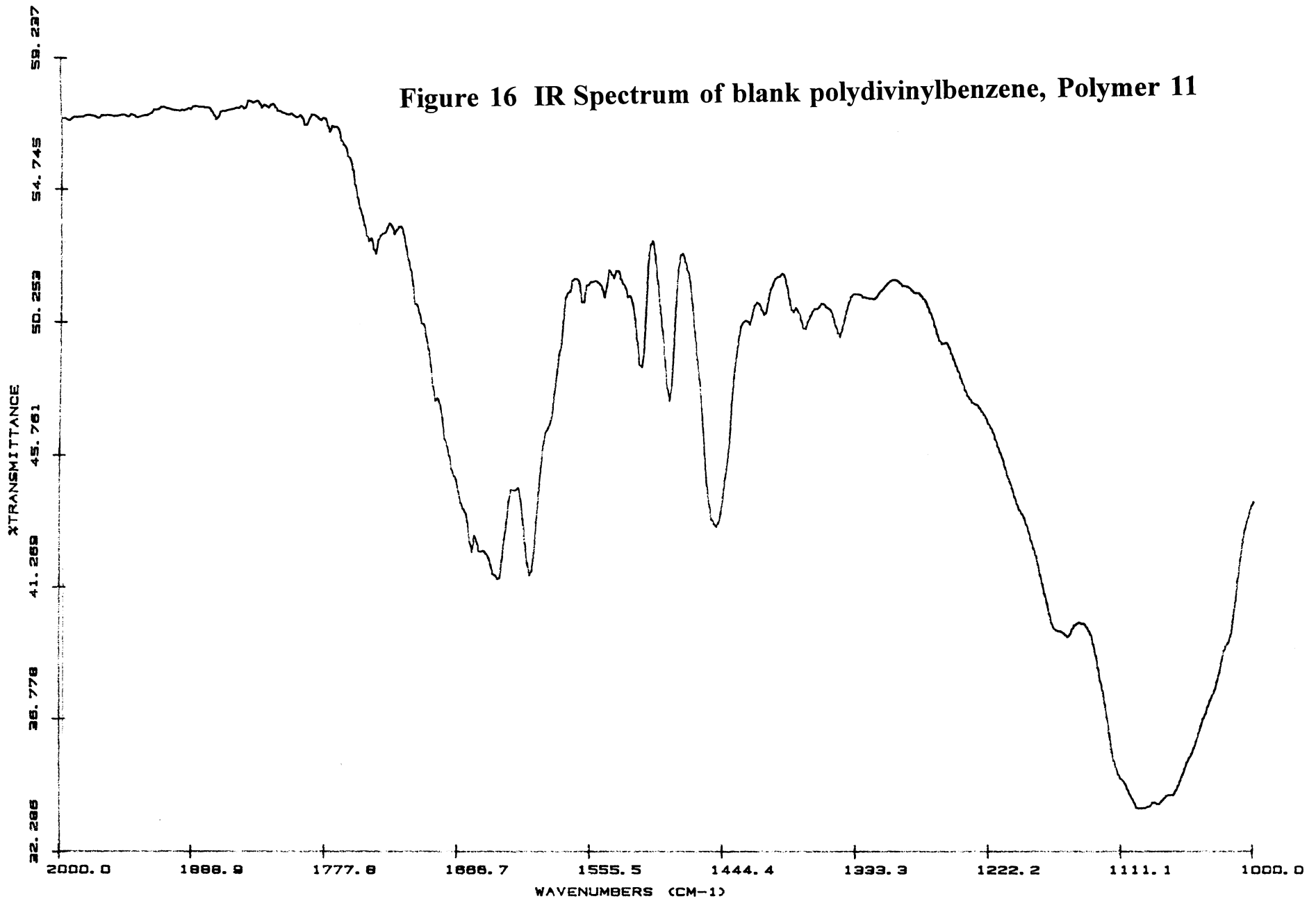


Figure 17 IR Spectrum of copolymer 4-nitrophenyl2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 12

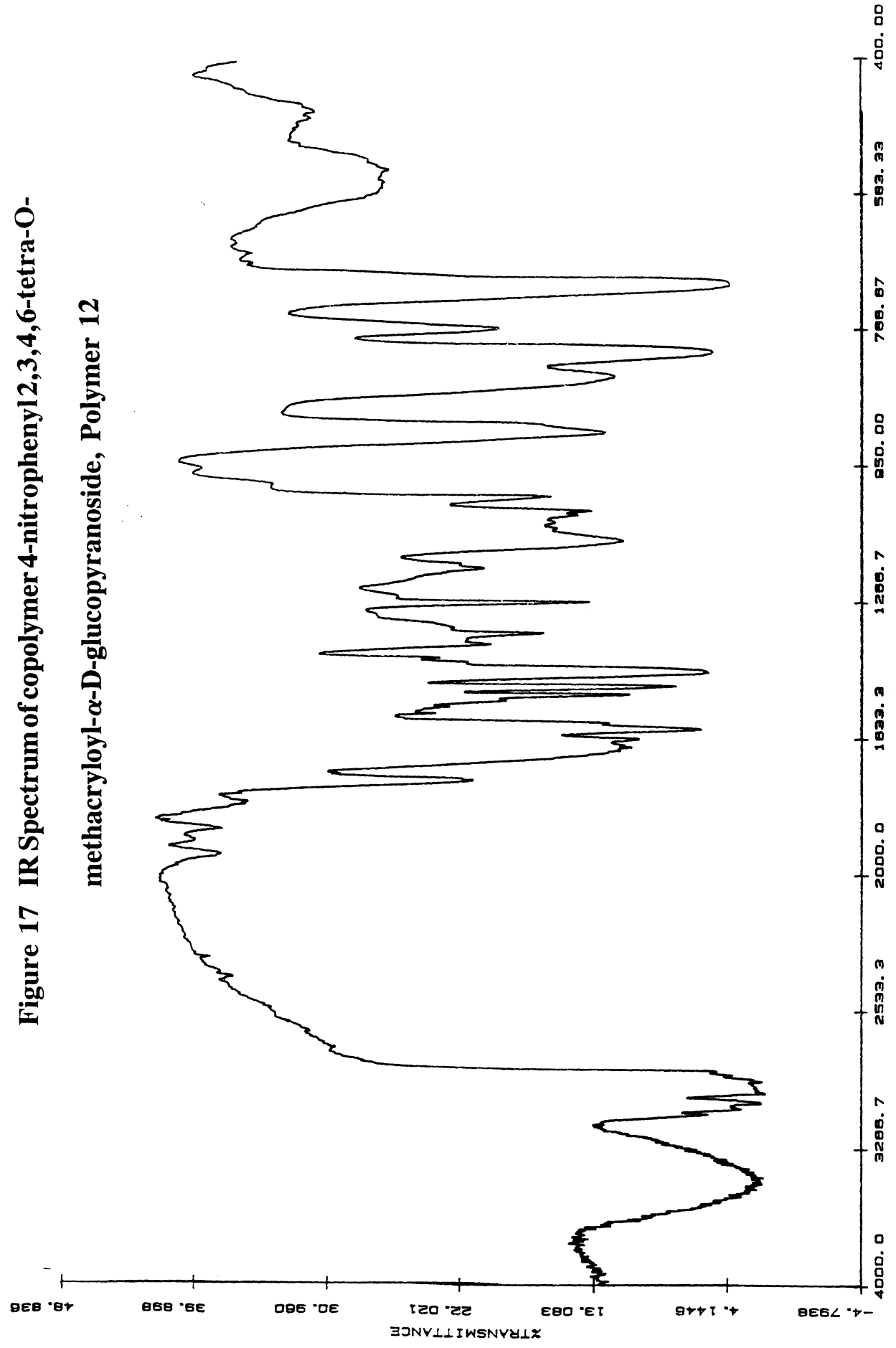


Figure 17 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 12

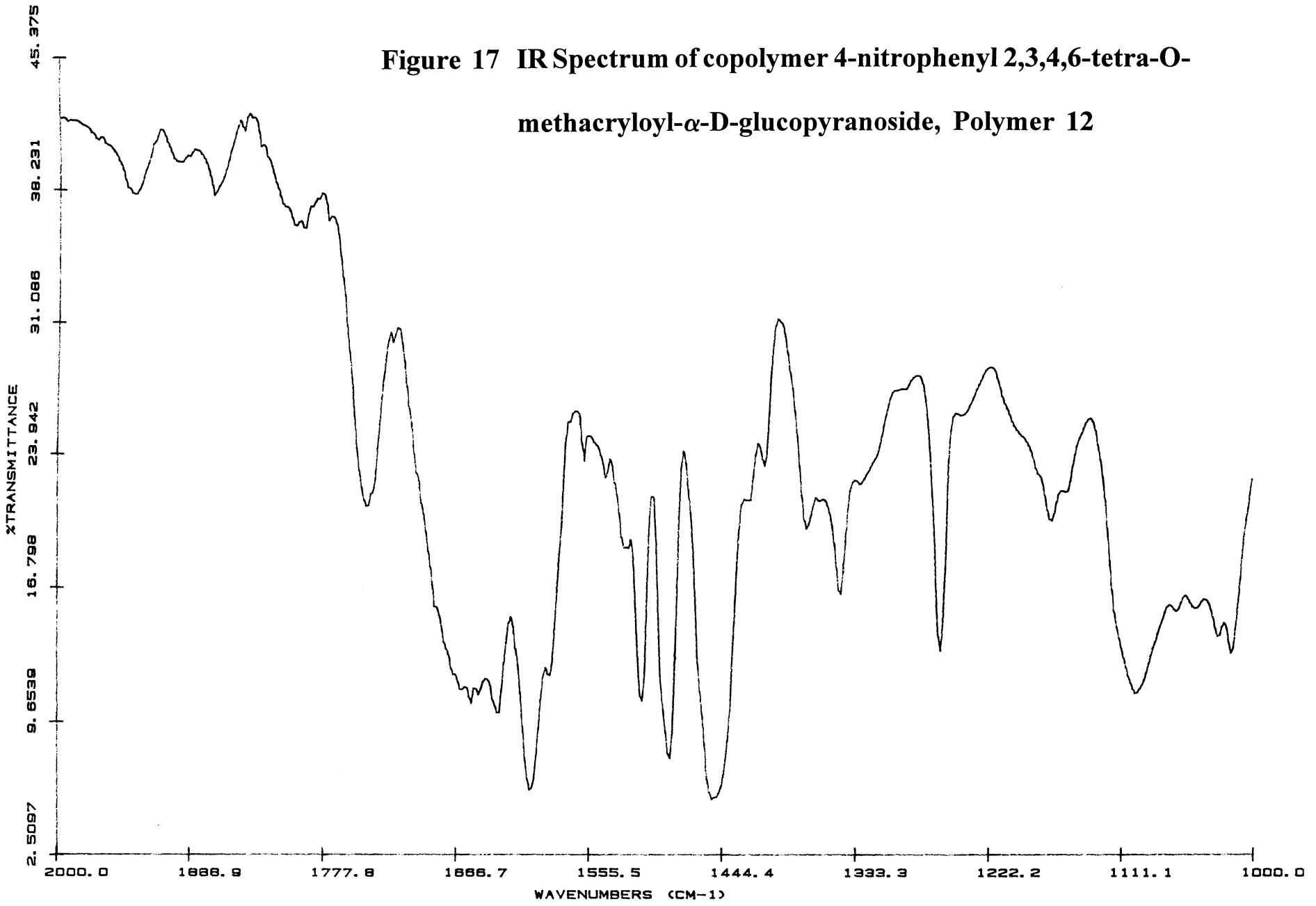


Figure 18 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 13

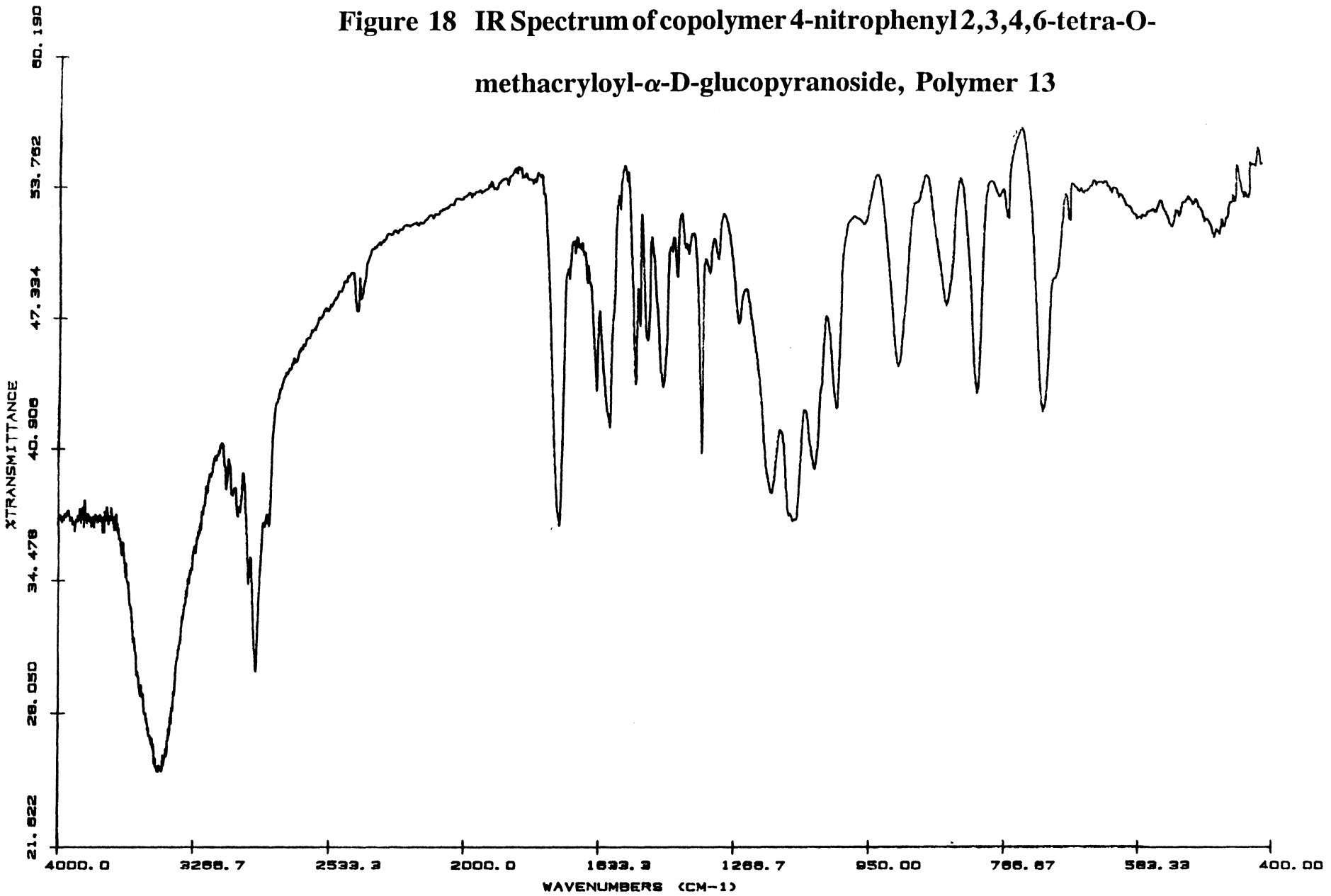


Figure 18 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 13

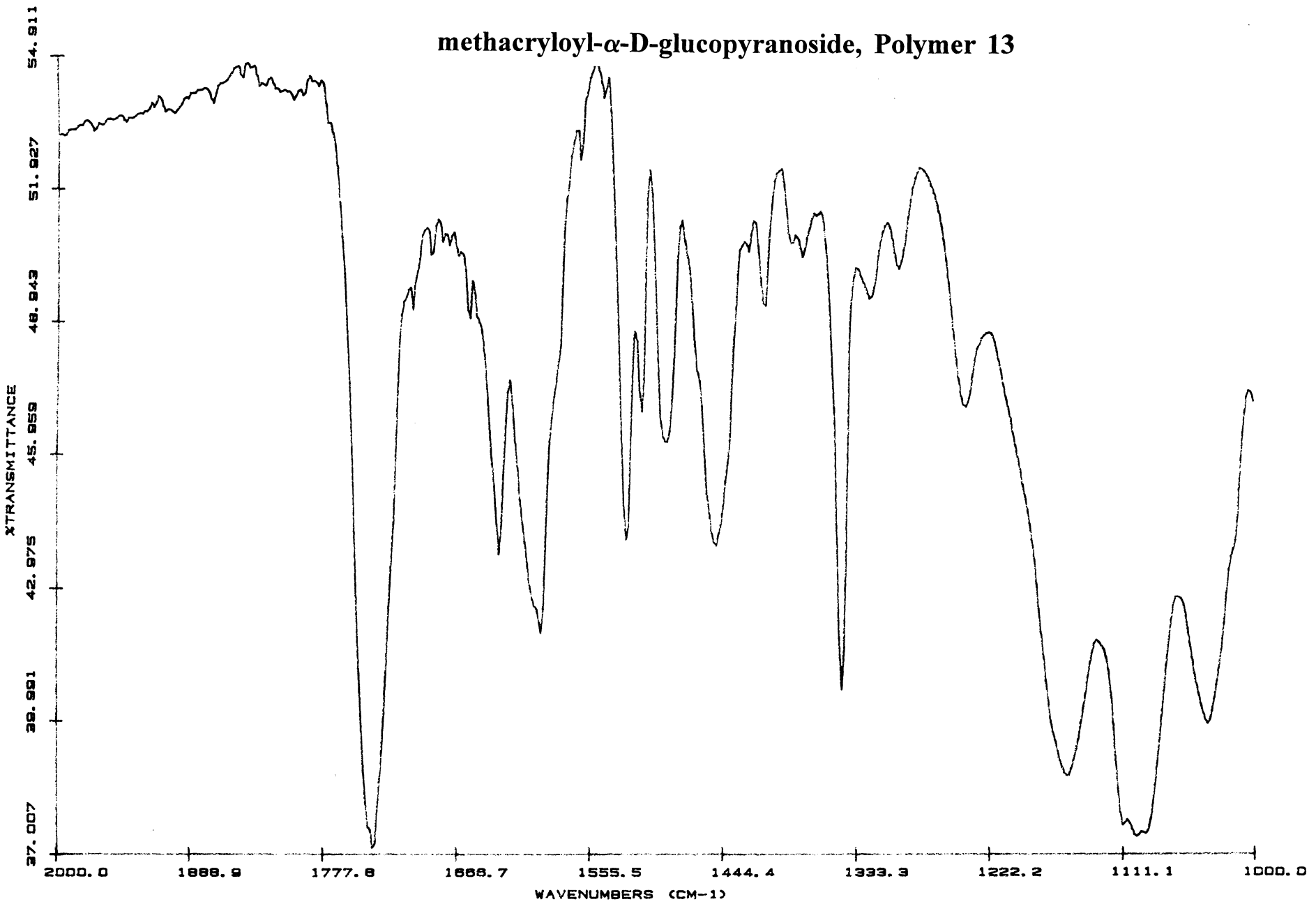


Figure 19 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 14

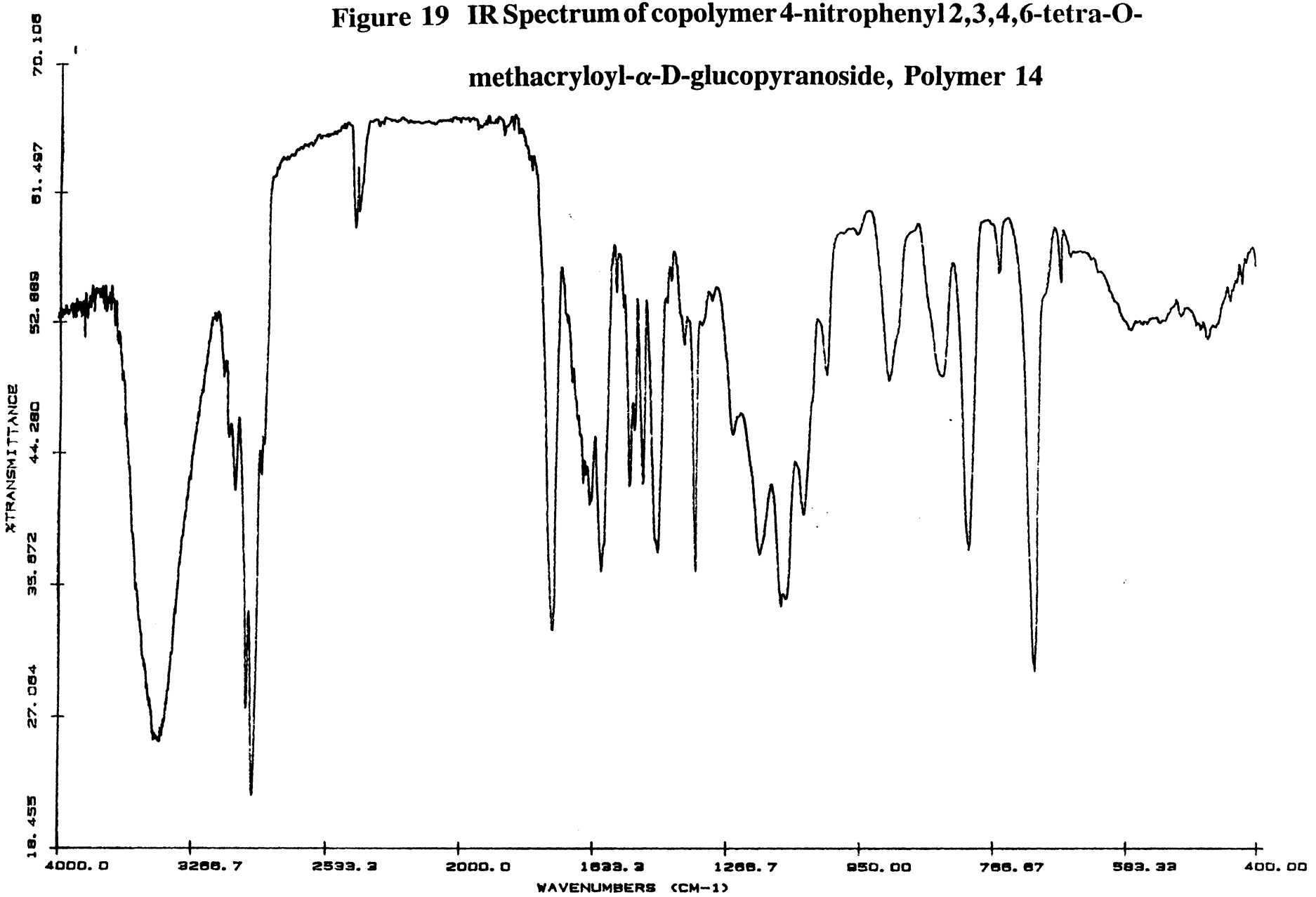


Figure 19 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 14

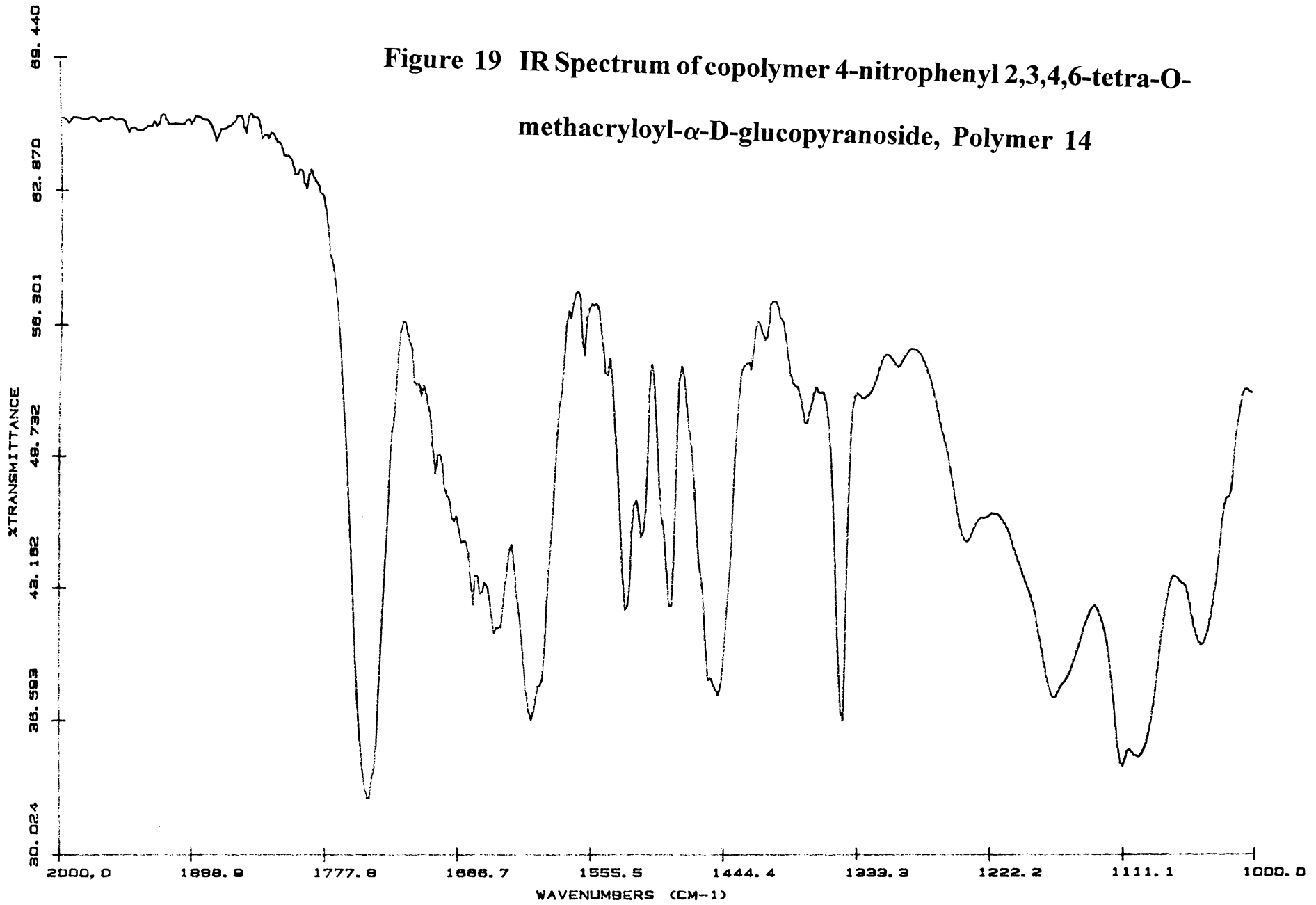


Figure 20 IR Spectrum of blank polydivinylbenzene, Polymer 15

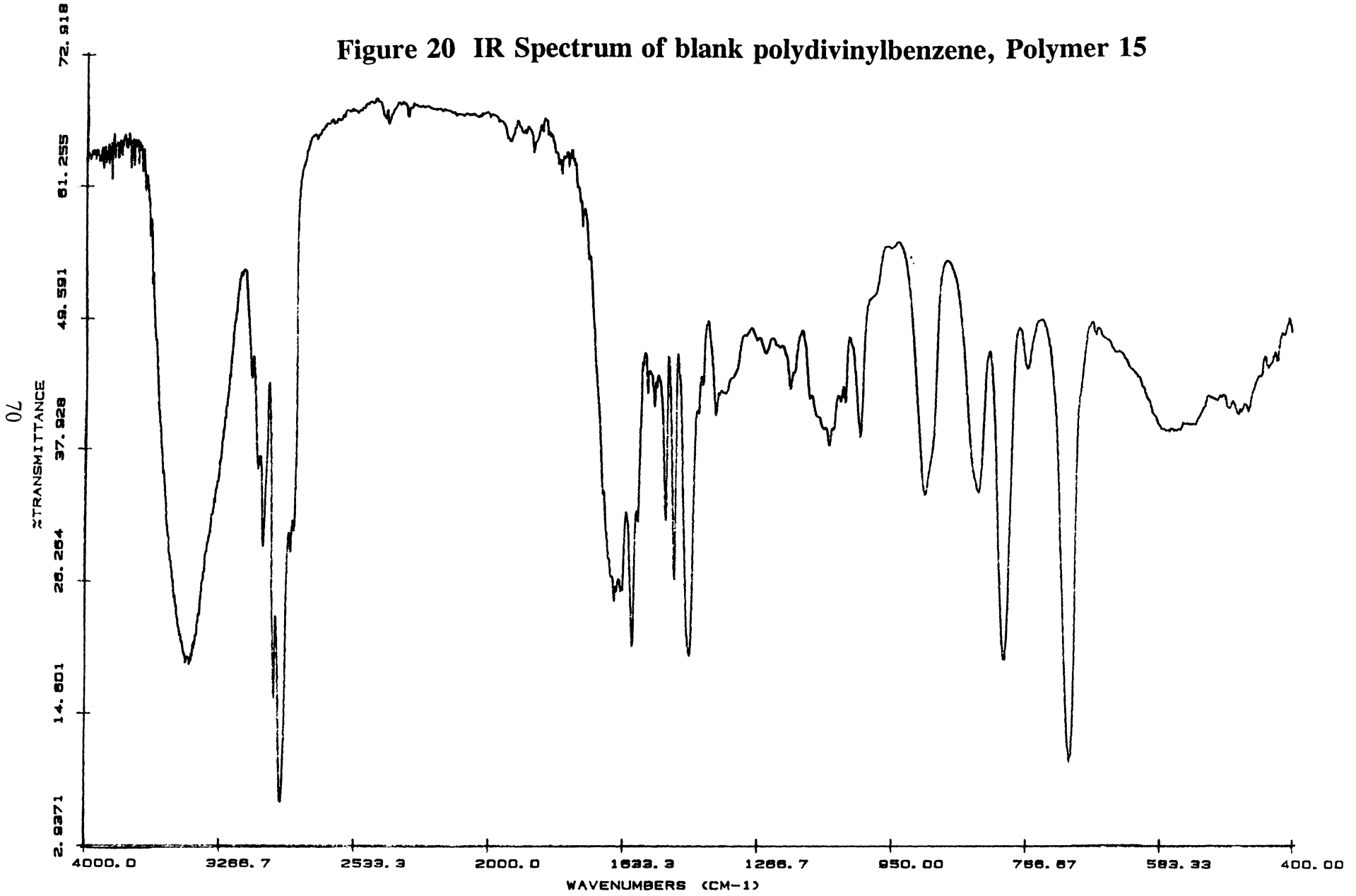


Figure 20 IR Spectrum of blank polydivinylbenzene, Polymer 15

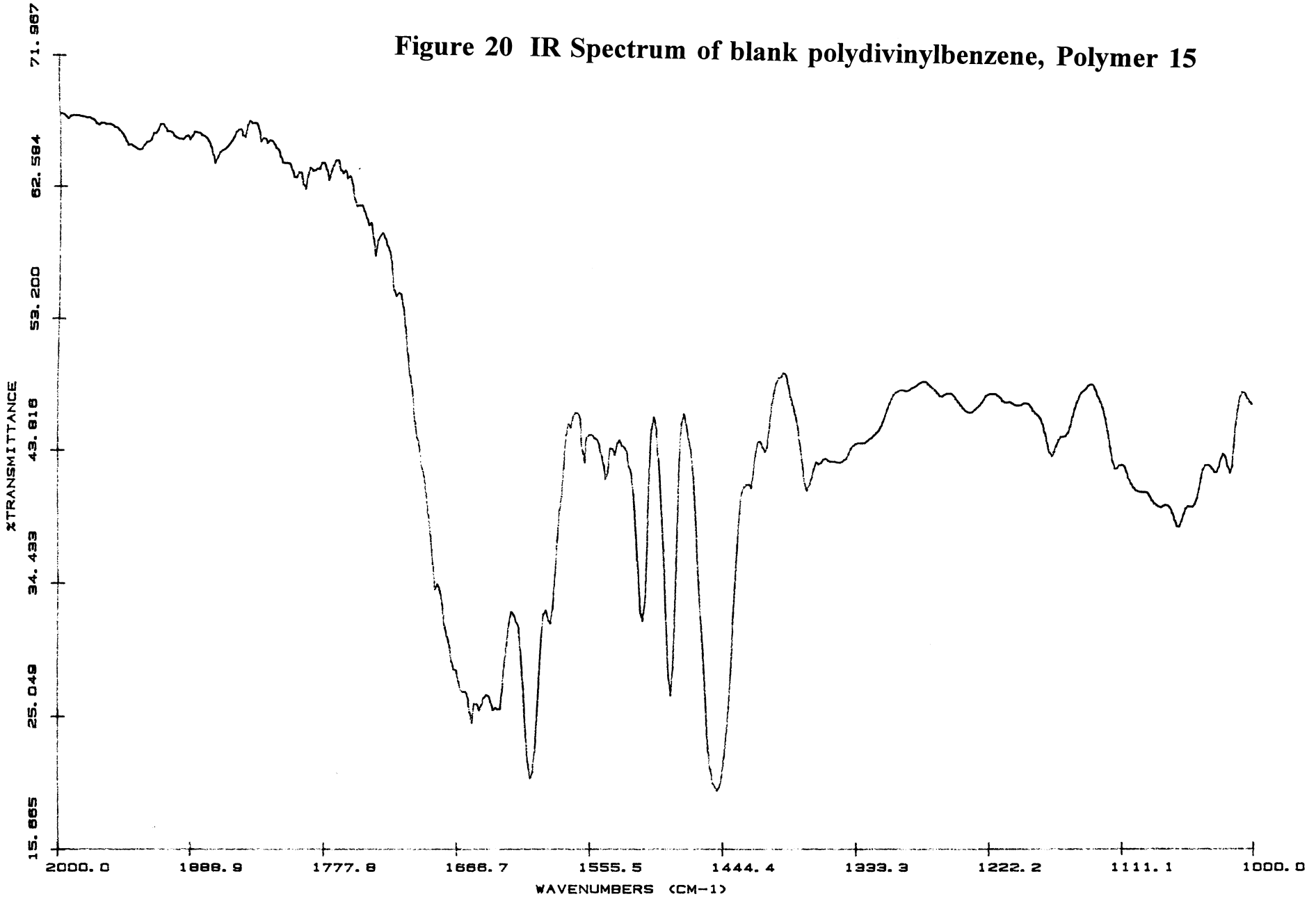


Figure 21 IR Spectrum of blank polydivinylbenzene, Polymer 16

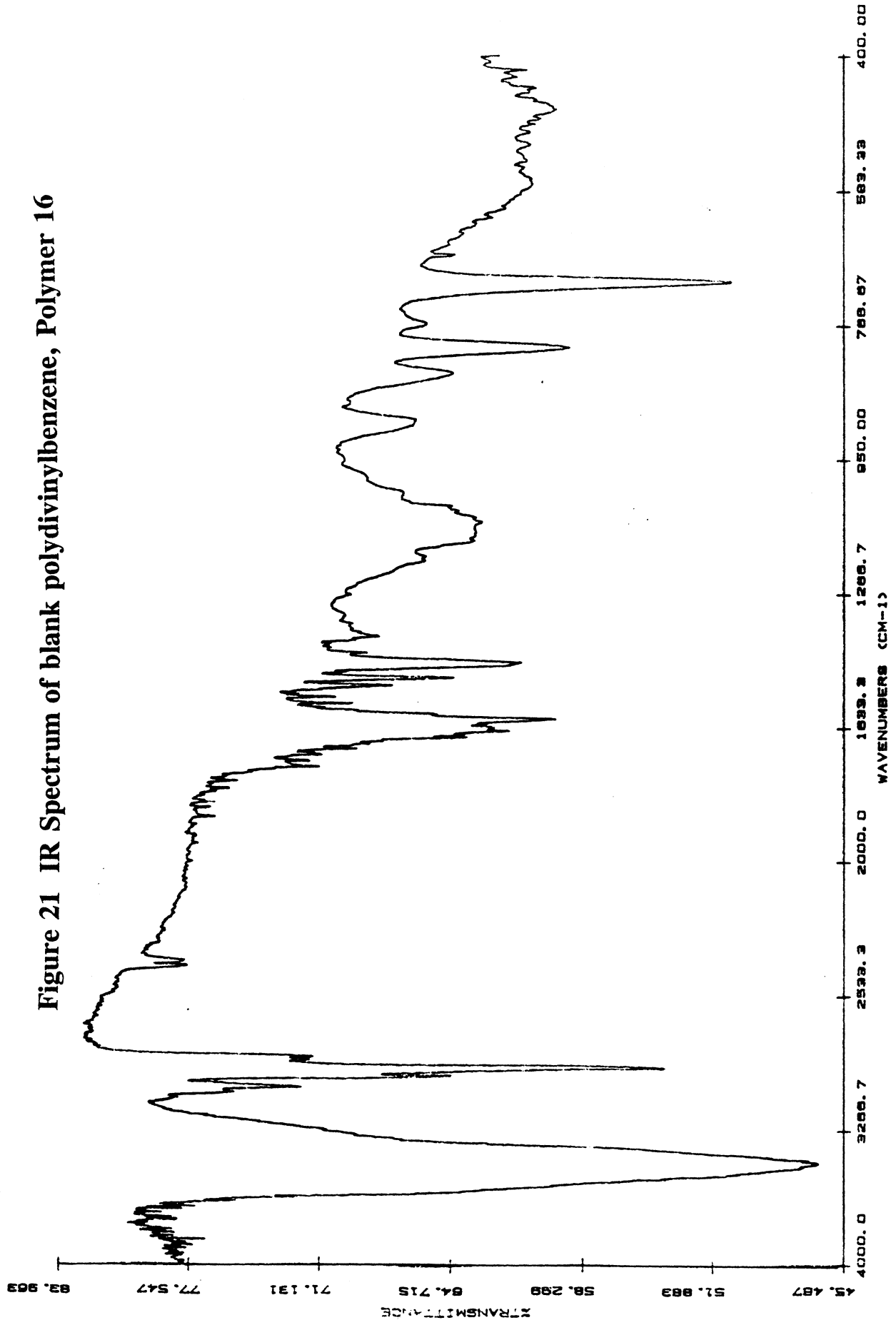


Figure 21 IR Spectrum of blank polydivinylbenzene, Polymer 16

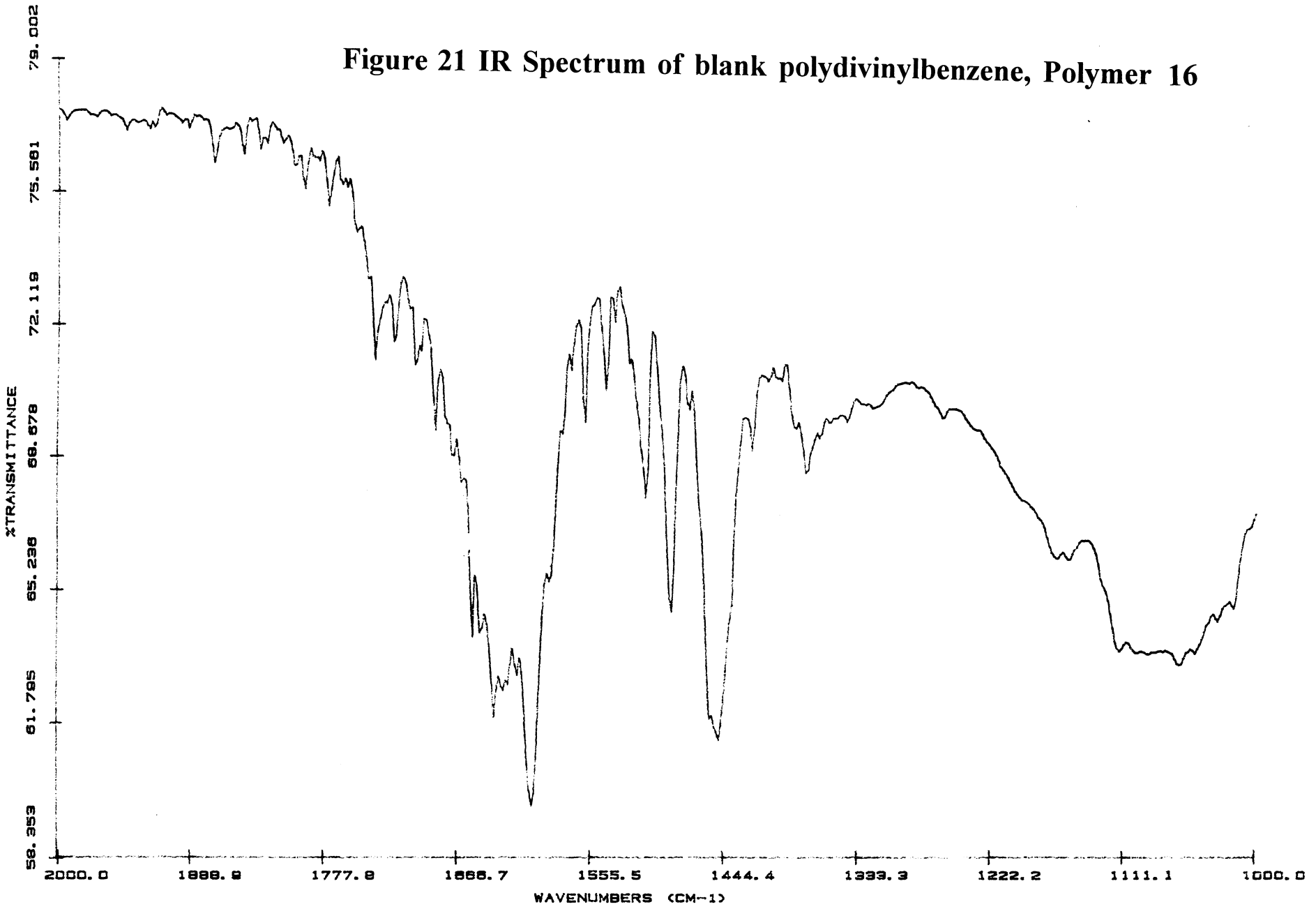


Figure 22 IR Spectrum of blank polydivinylbenzene, Polymer 17

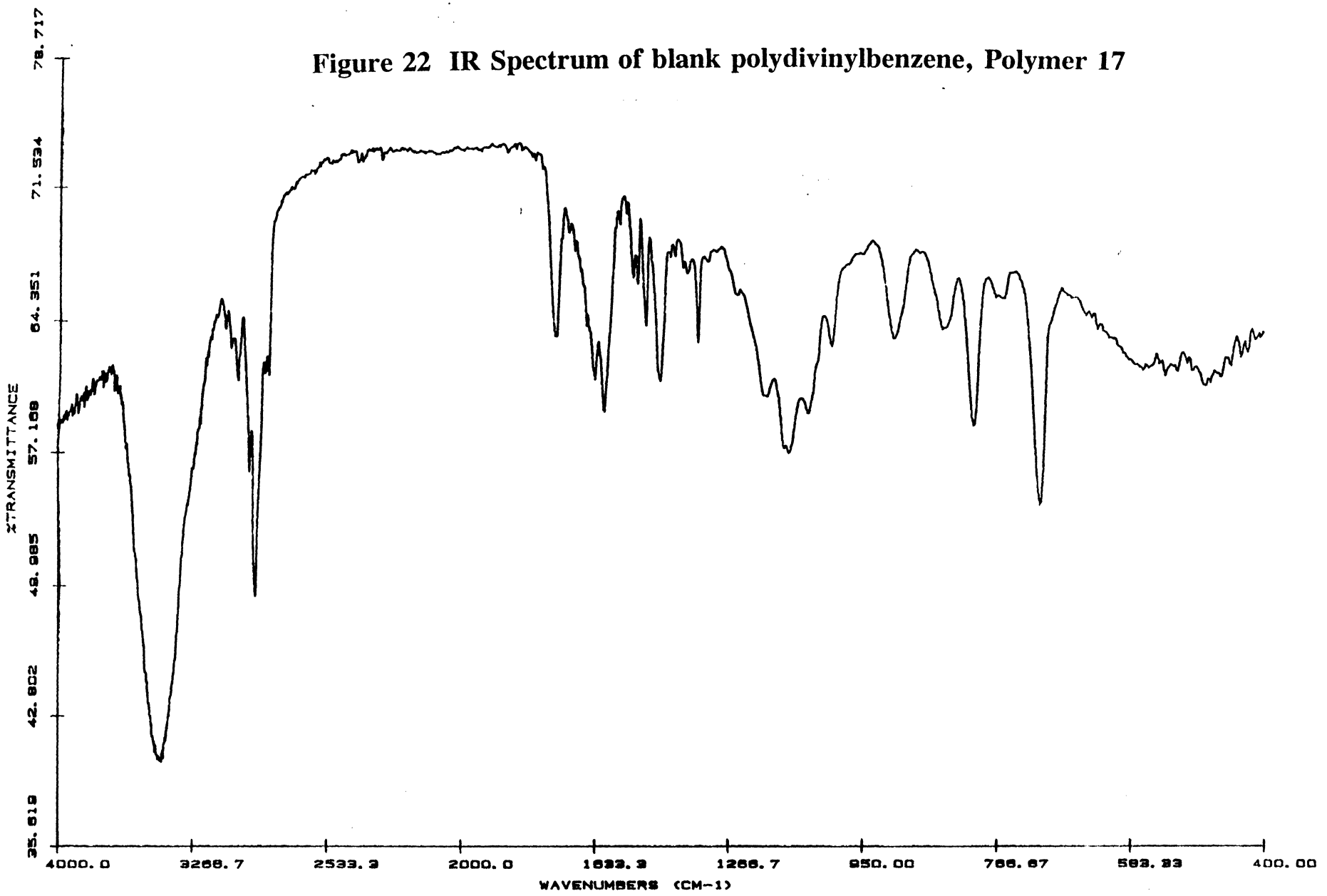


Figure 22 IR Spectrum of blank polydivinylbenzene, Polymer 17

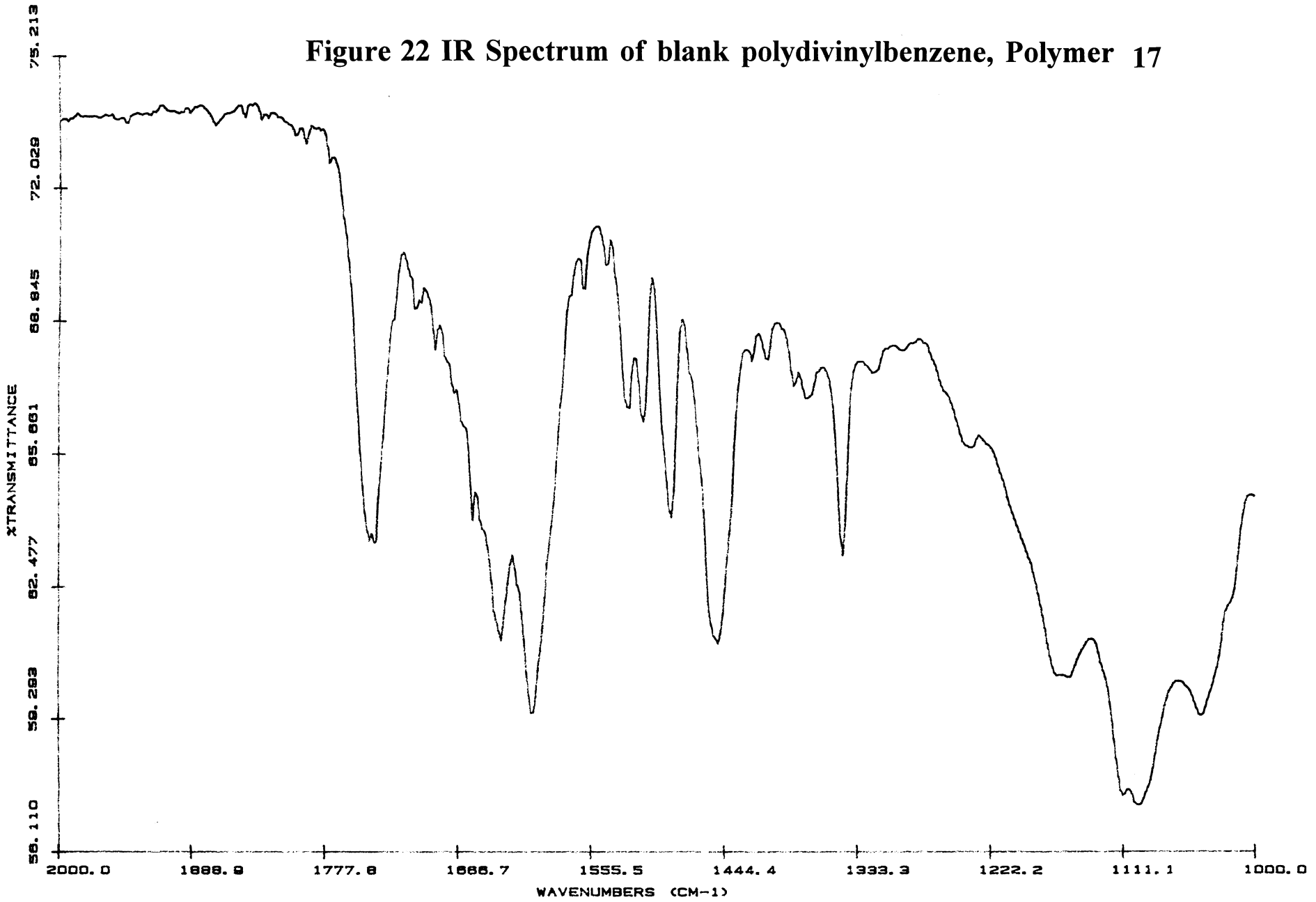


Figure 23 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 18

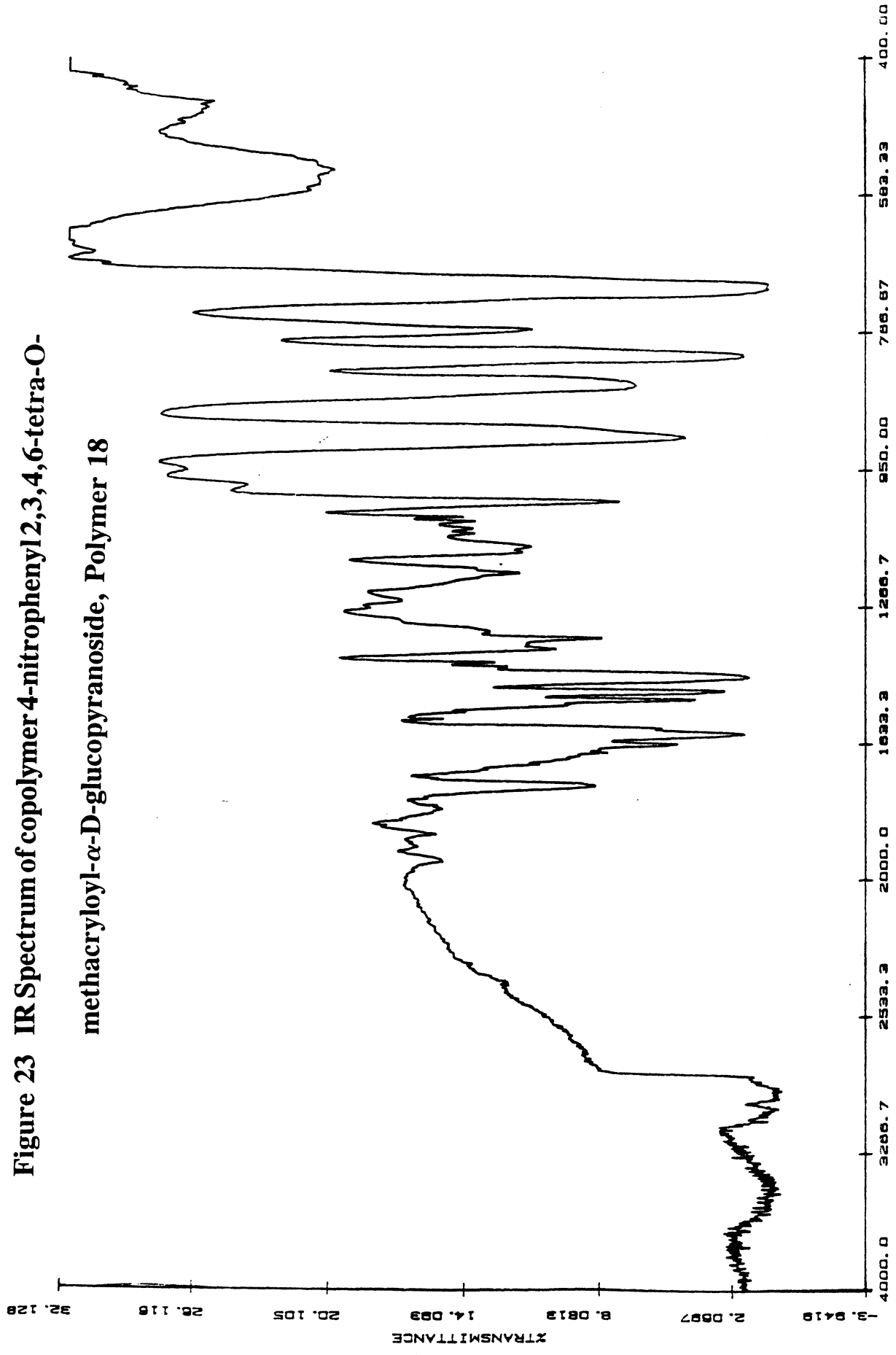
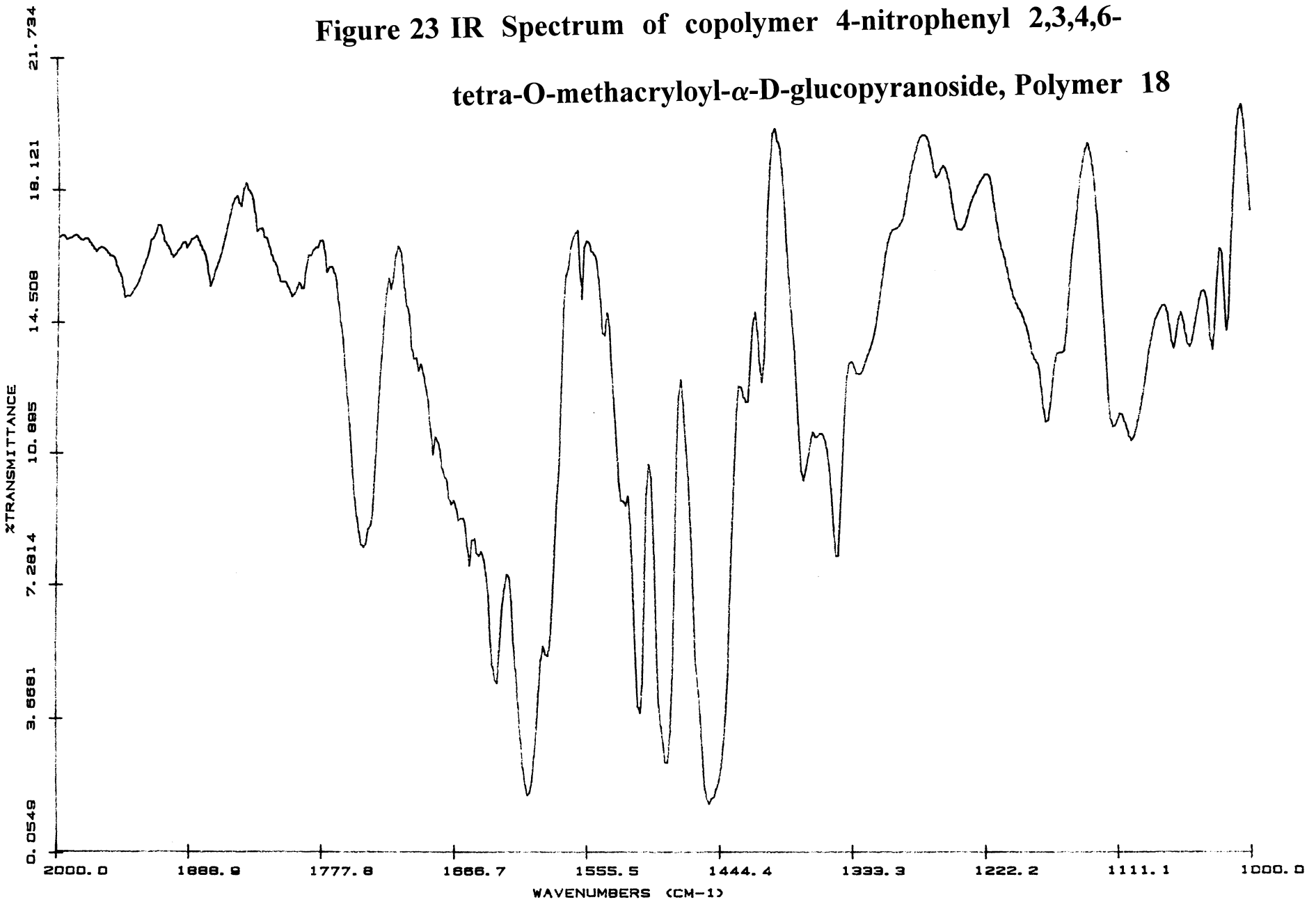


Figure 23 IR Spectrum of copolymer 4-nitrophenyl 2,3,4,6-tetra-O-methacryloyl-α-D-glucopyranoside, Polymer 18



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2. St. Augustine High School, Zimbabwe	1984 1985	"A" Level
3. Comenius University, Czechoslovakia	1986 1992	M.S. Organic Chemistry
4. Eastern Illinois University, U.S.A.	1992 1994	M.S. Chemistry