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PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	15MAY92	technical; 01JUN91 to 31MAY92

4. TITLE AND SUBTITLE

Novel Crosslinked Guest-Host System with Stable Second Order Nonlinearity

5. FUNDING NUMBERS

C: N00014-90-J-1148

R&T Code: 4132016

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8. PERFORMING ORGANIZATION REPORT NUMBER

1148-92-01

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research-Chemistry Division
Department of the Navy
Arlington, Virginia 22217-5000

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

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13. ABSTRACT *(Maximum 200 Words)*

An epoxy based nonlinear optical (NLO) polymeric material incorporating 4-(4'-nitrophenylazo) phenylamine has been synthesized and subsequently functionalized with acryloyl groups. A glass transition temperature (Tg) of 108°C and a degradation temperature (air) of 251°C were recorded. After crosslinking at 160°C for 2 hours, the Tg of the polymer increased to 146°C. In order to increase the nonlinear optical chromophore concentration and the crosslinking density, the crosslinkable NLO dye, 2,4-acryloyloxy (4'-phenylazo nitrobenzene), was processed and poled in this epoxy based NLO material matrix in a manner similar to a typical guest-host system, and thermally crosslinked under above condition in the poled phase. The crosslinked guest-host material was found to be amorphous with a Tg of approximately 132°C. It also exhibits a second order nonlinear optical coefficient d_{33} of 14.14 pm/V at a maximum doping level of 33% by weight of the NLO dye, and retains 93% of its original d_{33} value after being subjected to thermal treatment at 100°C for 168 hours. The behavior of the crosslinked polymer and the crosslinked guest-host polymer is discussed.

14. SUBJECT TERMS

epoxy based nonlinear optical polymer

15. NUMBER OF PAGES

24

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

OFFICE OF NAVAL RESEARCH

GRANT N00014-90-J-1148

R&T Code 4132016

Technical Report No. 92-01

Novel Crosslinked Guest-Host System with Stable Second Order Nonlinearity

by

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submitted to
Journal of Macromolecular Science-Pure and Applied Chemistry

University of Massachusetts Lowell
Department of Chemistry
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May 14, 1992

Novel Crosslinked Guest-Host System with Stable Second Order Nonlinearity

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Abstract

An epoxy based nonlinear optical (NLO) polymeric material incorporating 4-(4'-nitrophenylazo) phenylamine has been synthesized and subsequently functionalized with acryloyl groups. A glass transition temperature (T_g) of 108°C and a degradation temperature (air) of 251°C were recorded. After crosslinking at 160°C for 2 hours, the T_g of the polymer increased to 146°C. In order to increase the nonlinear optical chromophore concentration and the crosslinking density, the crosslinkable NLO dye, 2,4-acryloyloxy (4'-phenylazo nitrobenzene), was processed and poled in this epoxy based NLO material matrix in a manner similar to a typical guest-host system, and thermally crosslinked under above condition in the poled phase. The crosslinked guest-host material was found to be amorphous with a T_g of approximately 132°C. It also exibits a second order nonlinear optical coefficient d_{33} of 14.14 pm/V at a maximun doping level of 33% by weight of the NLO dye, and retains 93% of its original d_{33} value after being subjected to thermal treatment at 100°C for 168 hours. The behavior of the crosslinked polymer and the crosslinked guest-host polymer is discussed.

INTRODUCTION

Enhanced temporal stability of second-order NLO properties in a poled polymer system can be obtained when a certain degree of crosslinking is introduced [1-4]. In the crosslinked polymer, the NLO moieties are covalently bound into a rigid polymer network and are, therefore, much less likely to relax to random orientation. Such an approach was first reported by Eich et al. [2] in an epoxy system in which the NLO moieties are incorporated either in the multi-functional epoxy or amine components.

A new class of photo-crosslinked systems has been achieved by a *variation on the guest-host approach* [5-7]. The guest NLO molecules and host polymer contain functionalized groups through which crosslinking may be introduced. The system can be photo-crosslinked in the poled state to yield a material with stable optical nonlinearity. A guest-host system containing a crosslinkable NLO dye and a thermally-crosslinkable NLO epoxy based polymer was chosen for the present investigation. Both the dye and polymer are functionalized with the same type of reactive groups. This approach is based on the intermolecular and intramolecular thermal-crosslinking reactions of a functionalized NLO dye and an epoxy prepolymer (figure 1). In this system, not only the NLO chromophore density is increased by adding the crosslinkable NLO dye, but the crosslinking density increases as well.

The second order susceptibility is directly proportional to the concentration of the NLO moieties, and the temporal stability is related to the degree of crosslinking in the polymer matrix. Thus, large and stable NLO properties are expected from these crosslinked polymers. In this study, we report our investigations on a new guest-host crosslinking system based on the epoxy of the Diglycidyl Ether of Bisphenol A and 4(4'-nitrophenylazo) phenylamine (Disperse Orange 3) functionalized with acryloyl groups, and the crosslinkable NLO dye, 2,4-acryloyloxy (4'-phenylazo nitrobenzene). The acryloyl group was chosen as the reactive functional group. At a reasonably high temperature (>140°C) rapid reaction between the acryloyl groups is anticipated without the aid of catalyst or initiator. Upon heating, the reactive epoxy polymer and functionalized NLO dye form

a crosslinked network. We report on the stability at 100°C and at room temperature (25°C) of the second order nonlinearity of the crosslinked polymer films. The linear and second-order nonlinear optical properties of poled and crosslinked polymer were measured at 1060 nm and are reported.

EXPERIMENTS

Materials

Chemical synthesis of functioalized epoxy polymer of Diglycidyl Ether of Bisphenol A and 4(4'-nitrophenylazo) phenylamine with the reactive acryloyl groups (BPAZO) is described elsewhere [3,8]. The chemical structure of the polymeric product is illustrated in figure 2. The crosslinkable NLO dye 2,4 acryloyloxy (4'-phenylazo nitrobenzene) (APAN) was synthesized as reported in the literature [8] (Figure 2).

BPAZO was dissolved in mixed propylene glycol methyl ether acetate and 1,4-dioxane (volume ratio 3:1) with a weight ratio of 1:10. The solution was spin-coated onto glass slides, quartz slides and KBr plates, respectively, and then baked at 50°C under vacuum for 12 hours. Typical thickness obtained was approximately 0.60 μm. Indices of refraction at 532 nm and 1000 nm were measured using an ellipsometer. The samples of crosslinked guest-host system, BPAZO/APAN were prepared in the same manner as BPAZO. The weight ratio of BPAZO to APAN was 2:1. If the ratio is higher than 2:1, immiscibility is apparent in the thin films of this guest-host material.

Instruments

The glass transition temperatures, T_g, and the reaction behavior of the polymers were obtained from differential scanning calorimetry using a TA Instrument DSC2910 at a heating rate of 10K/min. The isotrack technique of DSC was applied to obtain the optimum curing conditions. The thermal degradation temperatures (T_d) of the polymers were determined on a TA Instrument TGA2950

with a heating rate of 10K/min under air. UV/Vis spectra were recorded on a Perkin Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on a Mattson FTIR.

The poling technique used was corona poling in the wire to plane arrangement [9,10]. Thin films of the polymers were poled and cured simultaneously. The poling was started at a temperature 10°C below the T_g of the polymer and then increased by 10K/min. The crosslinking reaction proceeds reasonably fast only at temperatures above 140°C (this will be discussed in the thermal analysis section). When the poling temperature reached 140°C, the temperature was advanced at a rate of 1°C/min. The corona field was carefully controlled in order to avoid electrical breakdown due to the high conductivity of epoxy type materials. Thin films of the polymer were heated to a temperature at which the crosslinking is fast (approximately 160°C) with the electric field on. After a time sufficient to bring the T_g close to the curing temperature (2 hours), the sample was cooled to room temperature with the electric field on.

The second order nonlinear optical coefficient (d_{33}) of the poled thin film was measured by second harmonic generation (SHG) from 1060 nm laser radiation. The relaxation behavior of the second order nonlinear optical properties was studied by the decay of the second order nonlinear optical coefficient (d_{33}) as a function of time at both room temperature (25°C) and at 100°C after poling and curing. These measurements were made with a Q-switched Nd-YAG laser (Quantel 660A). The p-polarized incident beam was separated by a beam splitter. One of the beams was passed through the sample, and the other was passed through a y-cut quartz reference. Both transmitted fundamental waves were blocked using $CuSO_4$ solution. Two narrow band interference filters centered around 532 nm were used to allow the second harmonic (SH) beam to pass. The SH signals were detected by two photomultiplier tubes, one for the quartz reference and the other for the sample. The signals were amplified and averaged in a boxcar integrator (Stanford Research SR-250). Figure 3 shows the experimental set up for the SHG measurement.

RESULTS AND DISCUSSION

Thermal analysis

TGA scans at 10K/min of BPAZO, APAN, and BPAZO/APAN (weight ratio 2:1) are shown in figure 4. The degradation temperatures, as taken from the onset point of the step transition, are 251°C, 187°C, and 197°C, respectively. The curing temperature was kept below 180°C to avoid degradation.

A DSC scan at 10K/min of BPAZO is shown on the top of figure 5. The exothermic reaction (curing) starts at approximately 140°C. The DSC isotrack technique permits good control of constant temperature of the sample, and is used to optimize the curing conditions. High curing temperatures are necessary for high T_g systems because of low reaction rates after vitrification. However, curing and thermal degradation often compete at such high temperatures [11]. These two factors were taken into consideration in our search for the optimum curing conditions. When the sample of BPAZO was heated at 160°C for 2 hours, its T_g advanced from 108°C to 146°C (bottom of figure 5). On heating for another 2 hours at 160°C, the T_g of BPAZO remained unchanged. Similarly after the sample of BPAZO was heated at 170°C for 2 hours, its T_g advanced from 108°C to 148°C. On the other hand, upon heating the pristine polymer for 3 hours at 150°C, its T_g advanced from 108°C to only 136°C. Based on the information above, the optimum curing condition chosen for BPAZO and BPAZO/APAN is isothermal heating of the sample at 160°C for 2 hours (unless otherwise stated, this curing condition was used throughout the study).

DSC scans at 10K/min of a mixed sample, BPAZO/APAN (weight ratio 2:1) before and after curing are shown in figure 6 and figure 7, respectively. The curve for the pristine sample shows that the melting point of APAN is 140°C. On curing, the melting peak disappears and a T_g appears at about 132°C. This suggests that the crosslinkable NLO dyes have reacted after curing.

IR study of the chemical reactions

Upon heating, the BPAZO undergoes reactions that can be analyzed by IR spectroscopy. As shown in figure 8, after 2 hours of

heating at 160°C, the carbonyl absorption peak at 1722 cm^{-1} shifts to 1730 cm^{-1} and becomes slightly broader. This indicates that a certain extent of crosslinking has occurred. In addition, an absorption peak emerges at 1680 cm^{-1} after curing. This suggests that intermolecular hydrogen bonding exists in the cured sample. The hydrogen bonding weakens the C=O bond, resulting in absorption at lower frequency [12]. The absorption peaks of the major functional groups such as nitro (1338 cm^{-1}), phenyl (1601 cm^{-1}), and ether (1242 cm^{-1}) have decreased only slightly in intensity after curing (the methyl absorption peak (2964 cm^{-1}) as the reference). It is, therefore, concluded that little thermal degradation has occurred during curing.

For the BPAZO/APAN, as shown in figure 9, after 2 hours of isothermal heating at 160°C, the carbonyl absorption peak at 1730 cm^{-1} not only shifts to 1747 cm^{-1} but also becomes much broader. This suggests that a significant portion of the conjugated carbonyl groups are now non-conjugated. It was also observed that the absorption peaks of the major functional groups of the cured sample, such as nitro (1340 cm-1), phenyl (1599 cm-1), and ether (1238 cm-1), all decrease to some extent in intensity (the methyl absorption peak (2964 cm^{-1}) as the reference). This suggests that a certain amount of functionalized NLO dye either sublimed away or degraded during the curing process at 160°C.

Linear and nonlinear optical properties

The second order NLO properties of BPAZO and BPAZO/APAN have been characterized by second harmonic generation. The d_{33} values obtained for the 1064 nm fundamental wavelength are listed in Table I along with some linear optical properties. The poled and cured films have d_{33} values of 8.86 and 14.14 pm/V for BPAZO and BPAZO/APAN, respectively. The poled and crosslinked guest-host system, BPAZO/APAN has a higher d_{33} value because it has a higher NLO chromophore density than BPAZO.

The temporal stability at 100°C of second order nonlinearity after poling and crosslinking of BPAZO and BPAZO/APAN has been

investigated (Figure 10). The result clearly indicates that the poled and cured guest-host system, BPAZO/APAN, shows much better stability. Over 168 hours at 100°C, a reduction of 7% in d_{33} was observed for the poled and cured BPAZO/APAN. Most of this loss was in the first few hours of heating. On the other hand, a reduction of 35% in d_{33} was observed for the poled/cured BPAZO under same thermal treatment. As mentioned earlier, the T_g of BPAZO/APAN is 13°C lower than BPAZO. However, the crosslinking density of BPAZO/APAN is much higher than BPAZO because many more reactive sites (acryloyl groups) are available in the crosslinked guest-host system. More crosslinks between the polymer chains restrict the molecular motion of the segments and hence prevent the randomization of the ordered NLO molecules. In addition, the nonlinear optical coefficients (d_{33}) of the poled/cured BPAZO and BPAZO/APAN remained unchanged under ambient condition for at least 168 hours, time to which these measurements were carried out.

UV-Vis absorption characteristics of poled films

To investigate the absorption behavior as a function of time, the absorption spectrum was taken regularly over a 168 hour period under thermal treatment at 100°C for poled/cured BPAZO. An absorption peak at λ_{max}=463 nm existed before poling/curing. After poling/curing λ_{max} shifts to 447 nm with a decrease of absorbance. During the next 168 hours λ_{max} shifted further toward shorter wavelengths with a slight decrease in absorbance (Figure 11). In addition, an isobestic point is shown at 430 nm in figure 11. This implies that the polymer and perhaps the chromophore possibly undergoes a certain extent of conformation change during the thermal treatment at 100°C.

For BPAZO/APAN, there are two absorption peaks, λ_{max}=352nm, and λ_{max}=464 nm corresponding to APAN and disperse orange 3 dye chromophores respectively in the spectrum of the pristine sample (figure 12). The absorption spectrum was also taken regularly over a 168 hour period under thermal treatment at 100°C. Immediately after poling/curing, a decrease in absorbance was observed. In

addition, the two chromophores responded to the poling/curing process differently. Similar to the BPAZO case, the absorption peak of the disperse orange 3 chromophore shifted toward shorter wavelengths (the shoulder around 450 nm in spectrum (b)) after poling/curing. On the other hand, the absorption peak of the APAN dye chromophore shifted toward longer wavelengths, λ_{max}=388 nm, immediately after poling/curing. During the next 168 hours, the absorption spectrum remained almost unchanged. This result suggests that the dye/polymer system did not degrade or sublime throughout the whole period of thermal treatment.

CONCLUSION

Linear epoxy polymer containing disperse orange 3 dye and crosslinkable groups, and crosslinkable NLO dye molecules have been synthesized. The uncrosslinked guest-host system has a very high NLO chromophore concentration and good solubility in common organic solvents. The curing time for this system is relatively short (i.e. 2 hours) compared to a typical thermally-crosslinked epoxy [2] (approximately 16 hours). Highly stable second order nonlinearity at 100°C has been achieved through this crosslinked guest-host polymer. The d_{33} of BPAZO/APAN retains 93% of its original value even after the poled/cured sample is subjected to thermal treatment at 100°C for over 168 hours. It is concluded that the temporal stability of the NLO properties was significantly improved by increasing the crosslinking density of the polymer. This type of material was obtained through doping a crosslinkable NLO dye into a crosslinkable polymer matrix.

ACKNOWLEDGEMENT

The authors would like to thank J. Chen, S. Marturunkakul, J. Kemnitzer, J. Lee, S. Sengupta, and Dr. M. Kamath for fruitful discussions.

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Legend to the Table

Table I Optical properties of cured BPAZO AND BPAZO/APAN

Legend to the Figures

Fig. 1 Schematic for the preparation of stable second order nonlinear optical polymers.

Fig. 2 The chemical structure of (a) BPAZO and (b) APAN.

Fig. 3 Experimental set up for SHG measurement.

Fig. 4 Thermal degradation behavior of (a) BPAZO, (b) APAN, and (c) BPAZO/APAN.

Fig. 5 DSC Thermograms of BPAZO.

Fig. 6 DSC Thermogram of pristine BPAZO/APAN

Fig. 7 DSC Thermogram of cured BPAZO/APAN

Fig. 8 Infrared spectra of BPAZO, from top to bottom: pristine, cured.

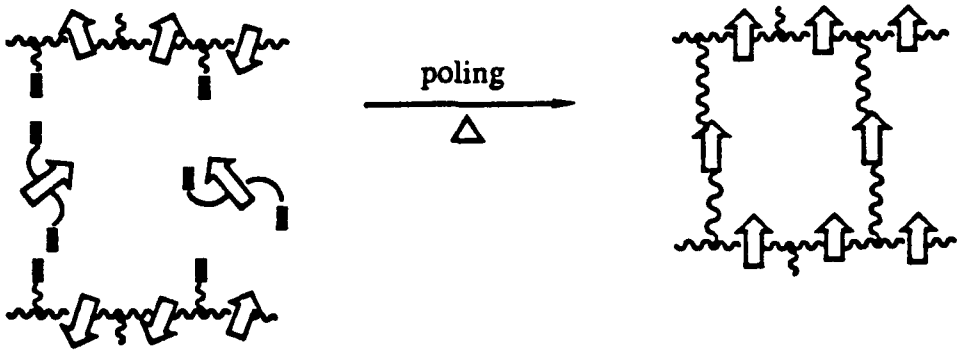
Fig. 9 Infrared spectra of BPAZO/APAN, from top to bottom: pristine, cured.

Fig. 10 Time behavior of second order nonlinear optical coefficient of poled/cured BPAZO and BPAZO/APAN. The samples subjected to thermal treatment at 100°C.

Fig. 11 UV-Vis absorption spectra of BPAZO, from top to bottom: (a) pristine, (b) right after poling/curing, (c) poled/cured samples subjected to thermal treatment at 100°C for 168 hours

Fig. 12 UV-Vis absorption spectra of BPAZO/APAN, from top to bottom: (a) pristine, (b) right after poling/curing, (c) poled/cured samples subjected to thermal treatment at 100°C for 168 hours

	BPAZO	BPAZO/APAN
Thickness (μm)	0.6	0.6
Refractive indice		
λ (μm)		
0.532	1.762	1.712
1.000	1.664	1.592
d_{33} (pm/V) at 1.06 μm	8.86	14.14
d_{31} (pm/V) at 1.06 μm	2.42	3.98



⇧ nonlinear moieties; ▮ reactive groups

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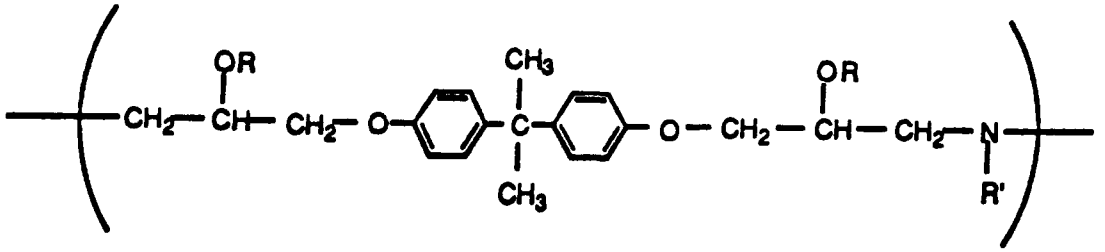
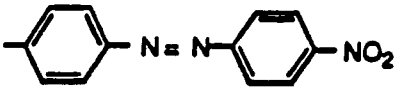


R = H or  ; R' = 

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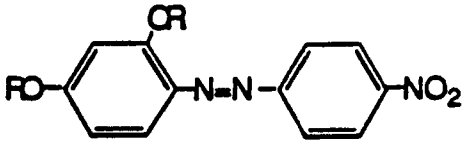

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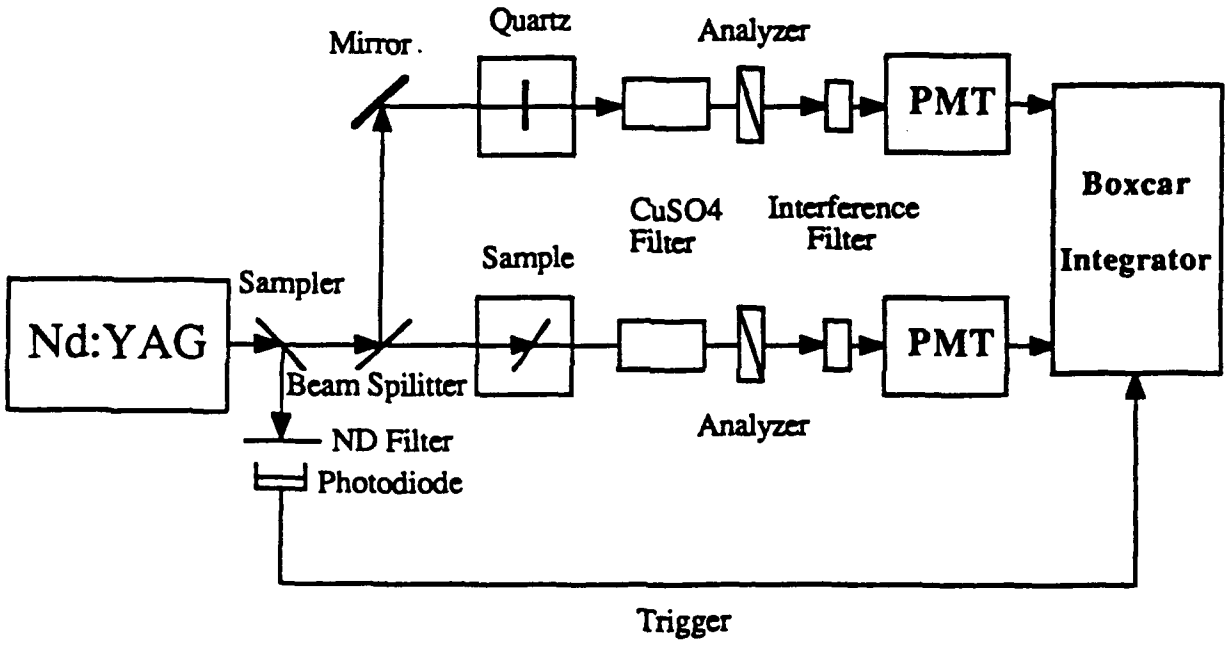
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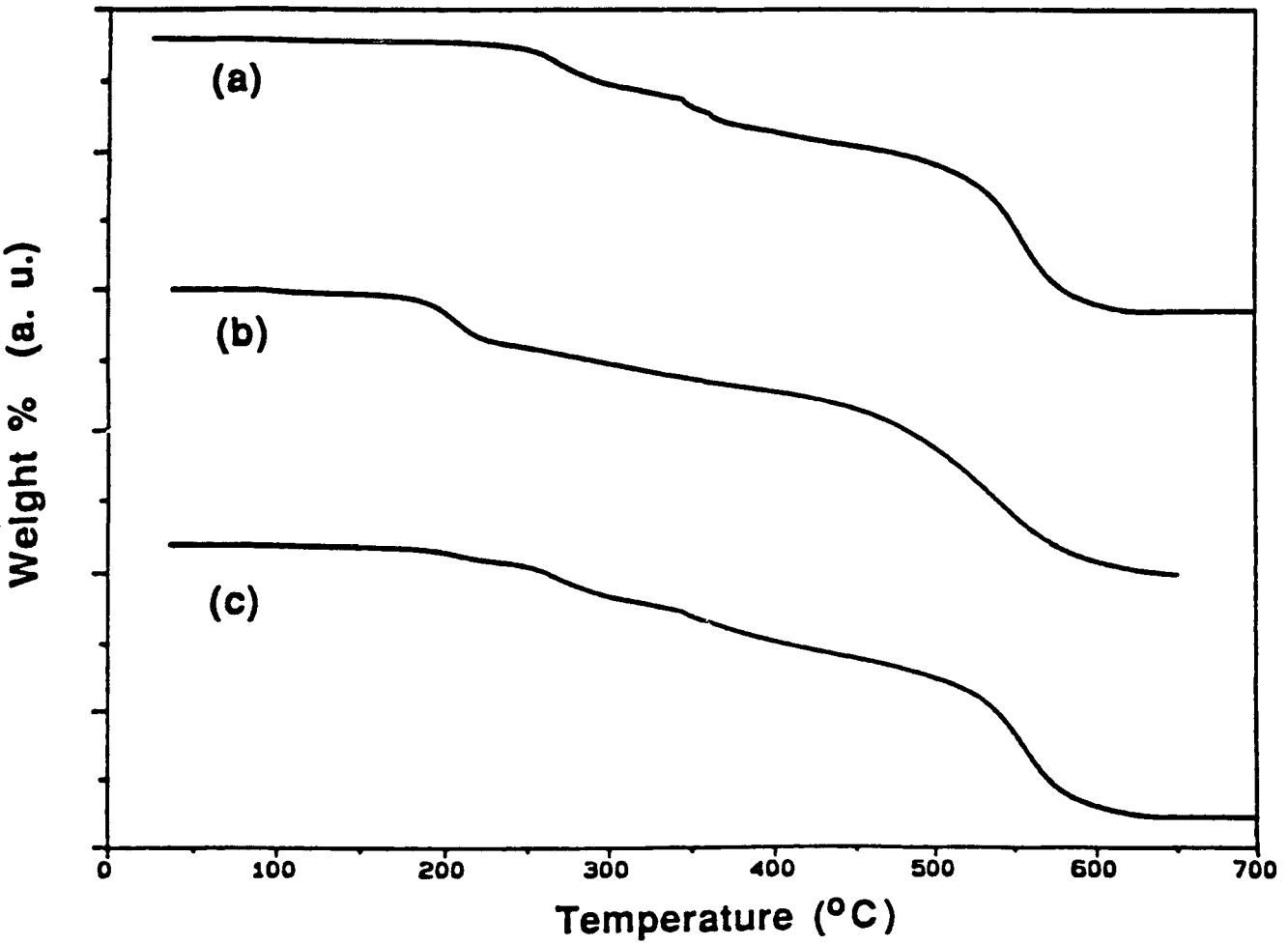
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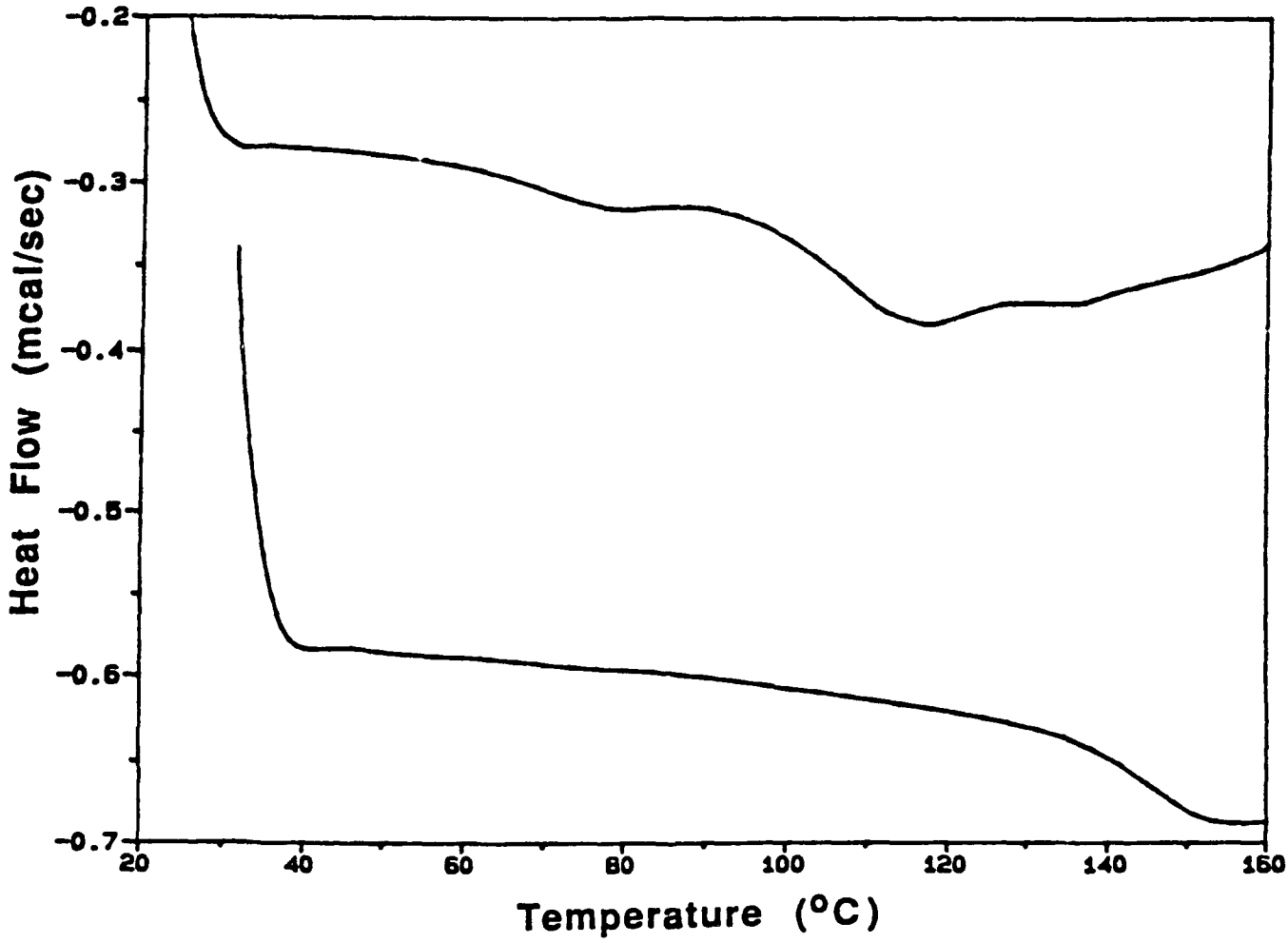
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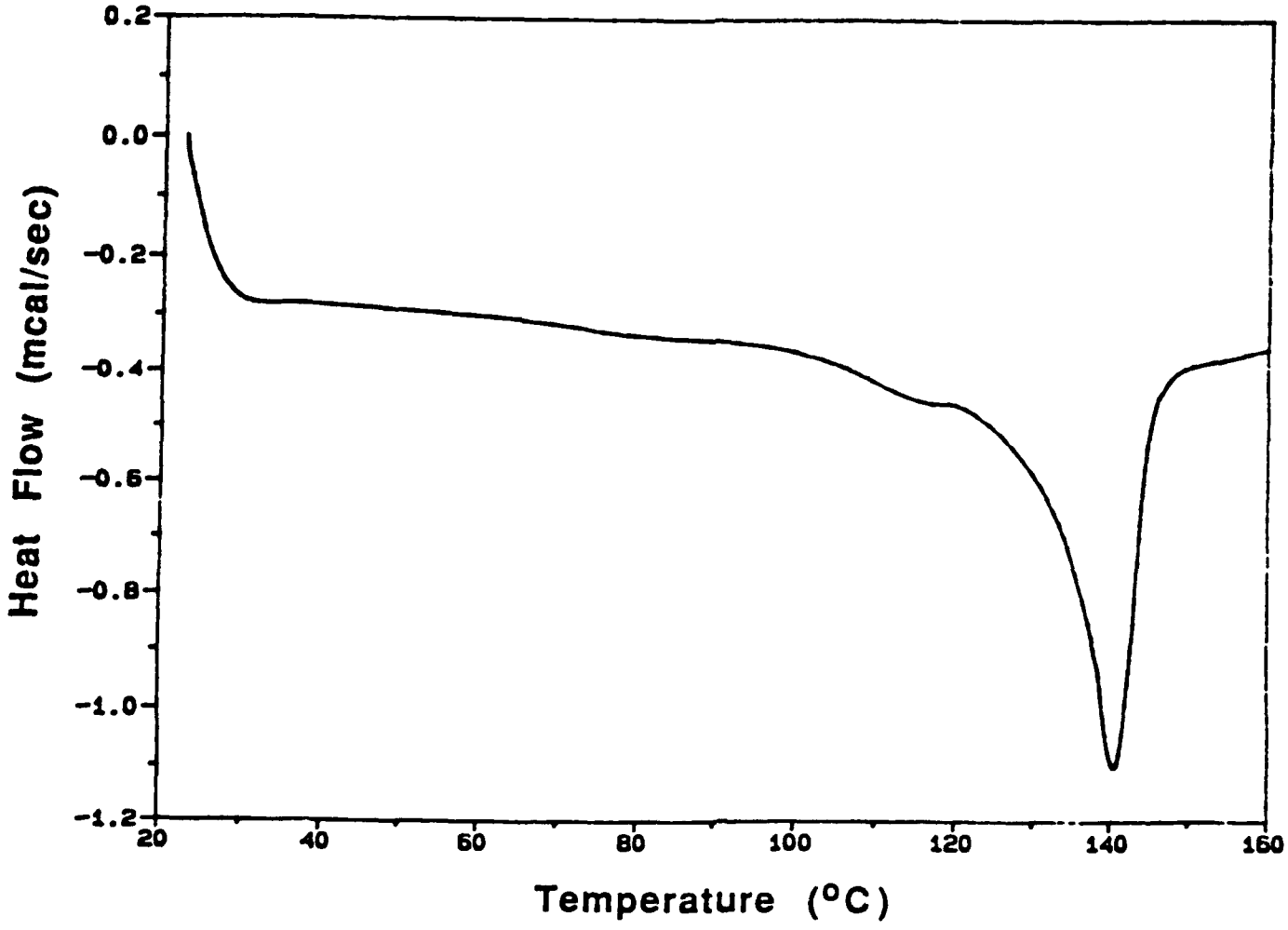
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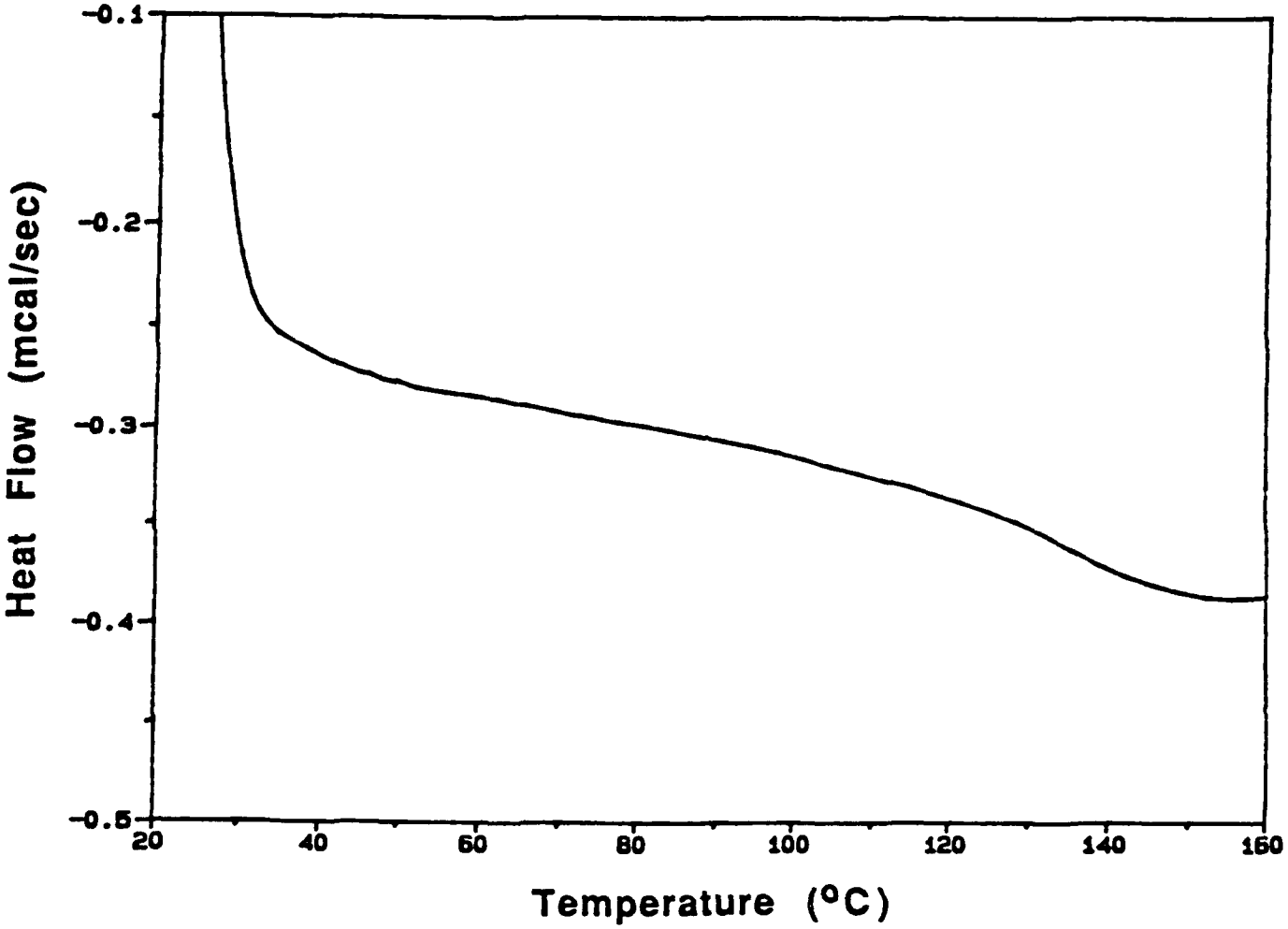
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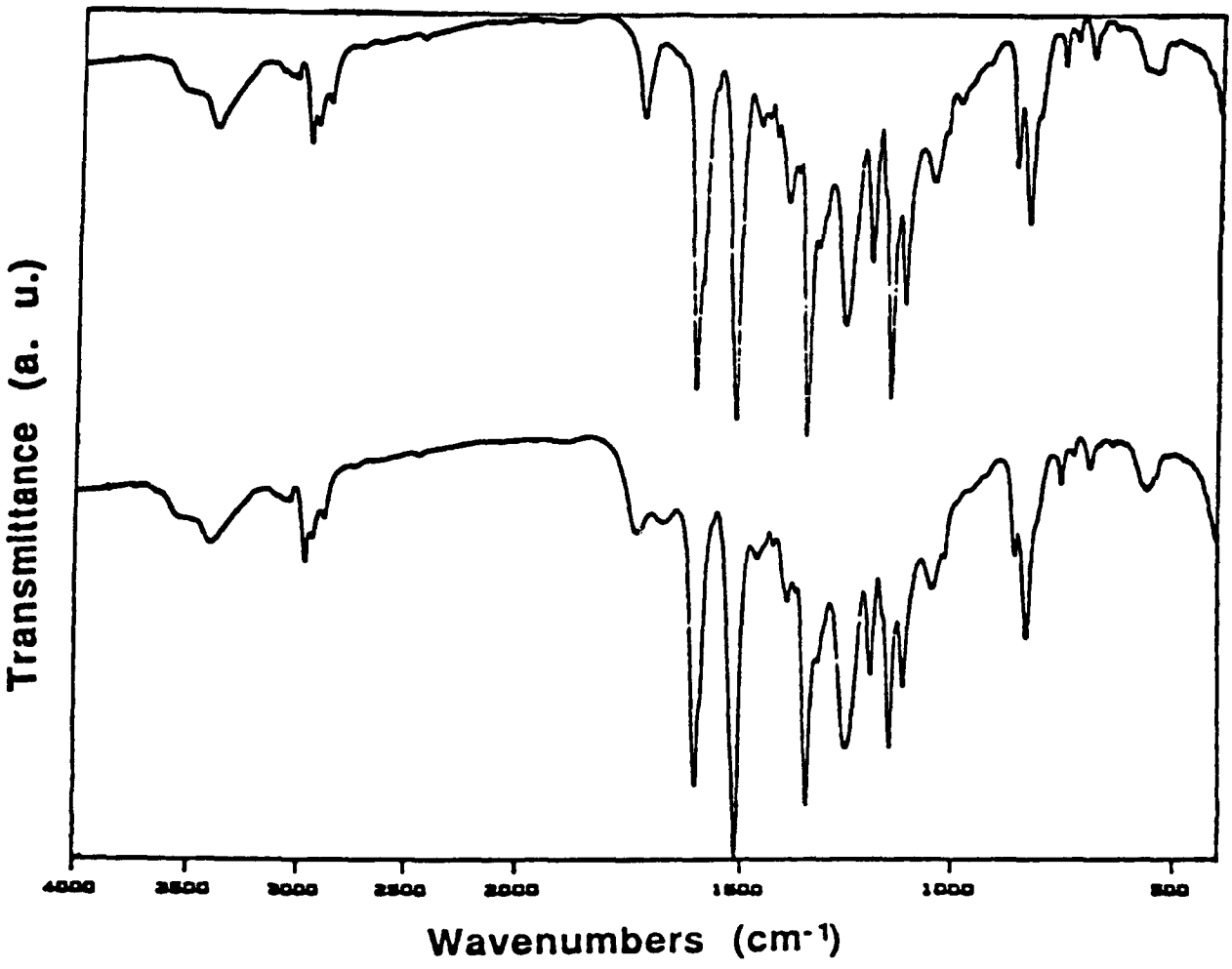
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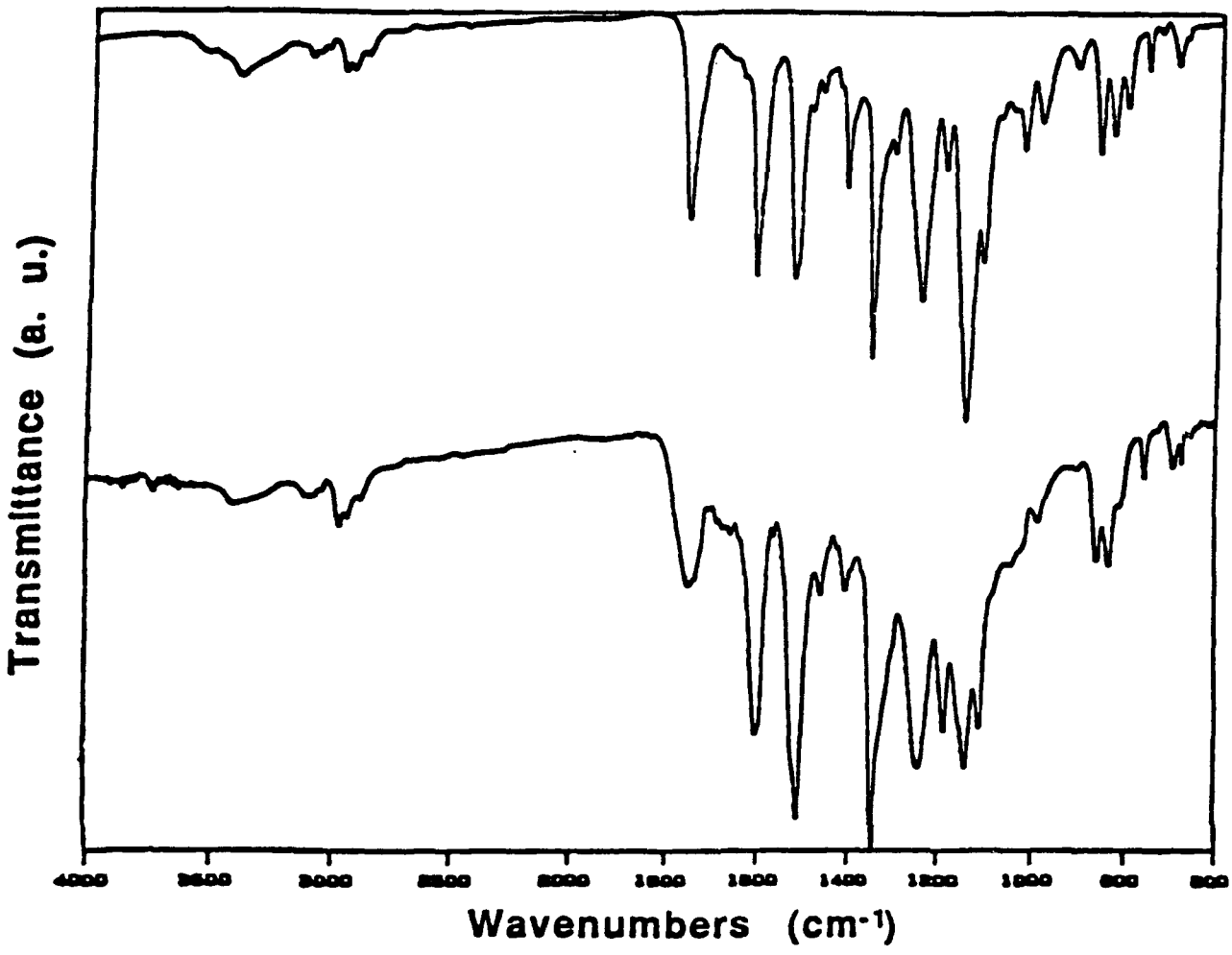
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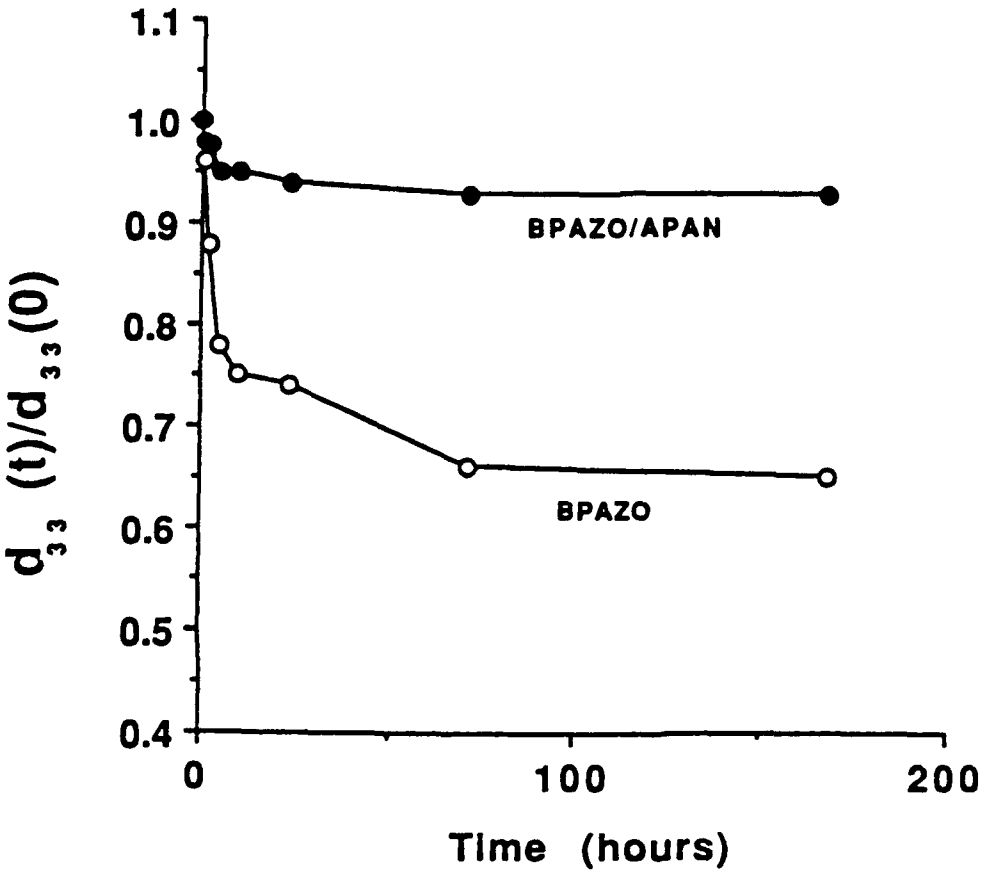
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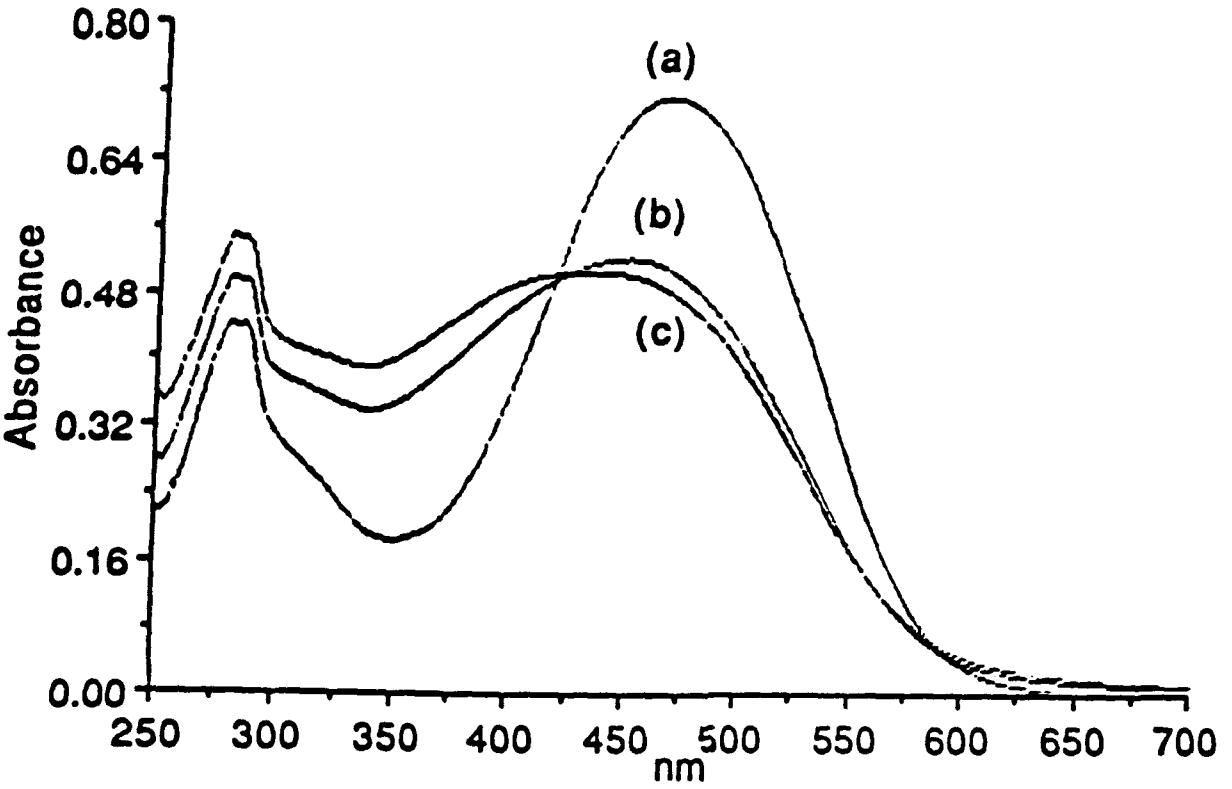
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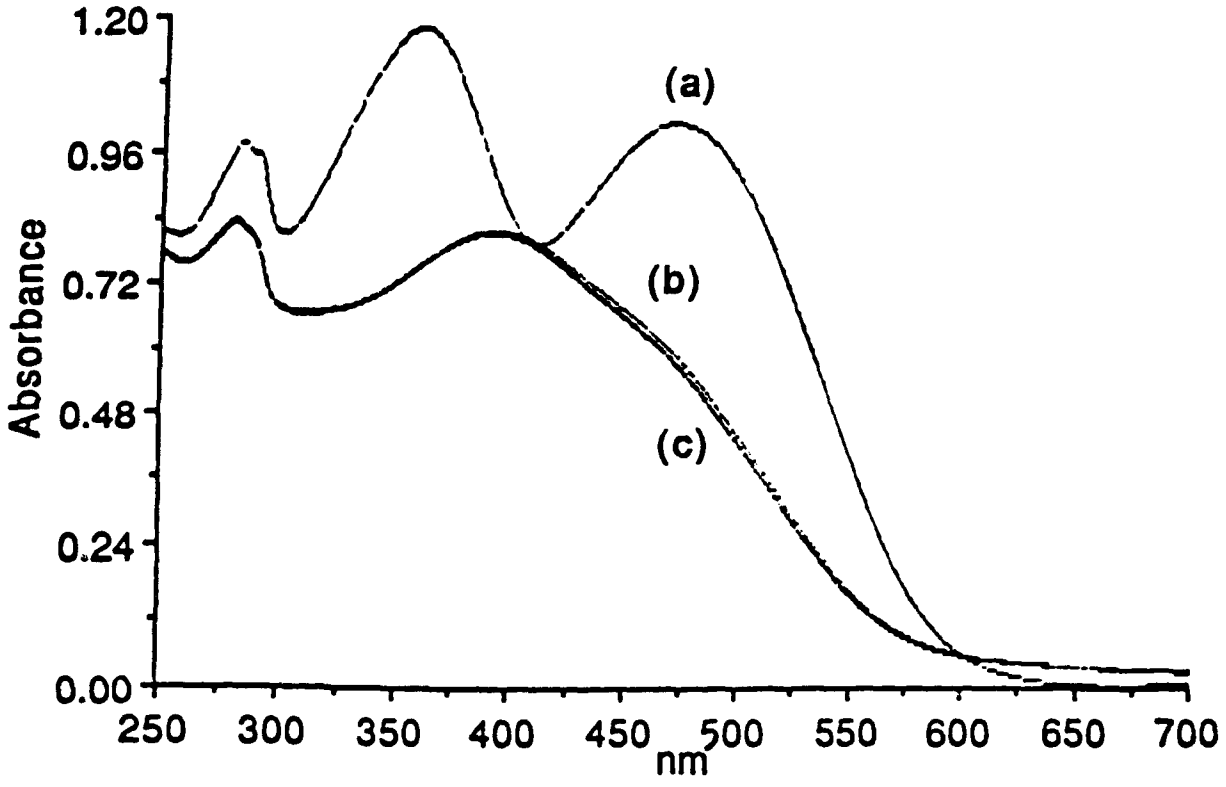
nm


1.20
0.96
0.72
0.48
0.24
0.00
Absorbance
(a)
(b)
(c)
250
300
350
400
450
500
550
600
650
700
nm

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