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**Synthesis and Physical Properties of
Liquid Crystalline Alkylisocyanate Copolymers**

by

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SYNTHESIS AND PHYSICAL PROPERTIES OF LIQUID CRYSTALLINE

ALKYLISOCYANATE COPOLYMERS

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INTRODUCTION

Liquid crystal polymers (LCP's) have wide applications ranging from electronic devices to ultra-high-strength materials. These intriguing polymers have been the subject of several review articles (1-3). Of the polymeric liquid crystal systems, poly(alkylisocyanates) are categorized as main-chain mesogenic polymers having a semi-rigid structure. Though the synthesis and characterization of poly(alkylisocyanates) were originally reported by Shashoua et al. (4,5), the liquid crystalline nature of these systems was investigated in greater detail by Aharoni and coworkers (6-11). These studies, involving various alkyl and aromatic isocyanate polymers, showed that while the alkylisocyanate homo and copolymers exhibited thermotropic liquid-crystalline behavior, they decomposed spontaneously above their melting points. Because of this decomposition property, the use of poly(alkylisocyanates) as thermotropic liquid crystals is limited.

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The aim of our study of poly(alkylisocyanates) was to improve their utility as model thermotropic LCP's; in particular, to widen the isotropic region without destroying their liquid crystallinity or solubility. A wide isotropic region is necessary for comparative rheological studies, for example. From the results of Shashoua (5) and Aharoni et al. (6,10,11) it was known that the temperature of melting (T_m) decreases in poly(alkylisocyanates) when the alkyl chain length of the monomer increases because the volume of the side chains prevents the highly polar main chains from packing closely. Moreover, copolymers of butylisocyanate with ethylisocyanate (12,13) and butylisocyanate with p-anisole-3-propylisocyanate (10) (50:50 mole ratio) were reported to exhibit increased thermal stability and wider range of mesomorphicity, respectively, than the corresponding homopolymers.

From these studies, it was considered probable that the introduction of irregularity into the side chains would lower the clearing temperature without changing the decomposition temperature. The irregularity can be achieved by synthesizing copolymers from long aliphatic side chain monomers with monomers containing shorter chains. We chose undecylisocyanate as our base polymer because it appears to be the upper limiting case of transition from mesogenic to non-mesogenic polymers. Here, we report the synthesis of homo and 50:50 copolymers of undecylisocyanate with propyl, butyl, hexyl and octylisocyanates. These polymers were characterized using FT-IR, TGA, DSC, Thermal Optical Analysis (TOA), Dynamic Mechanical Analysis (DMA), and tensile testing.

EXPERIMENTAL

Materials

n-Propylisocyanate (Aldrich), n-ethylisocyanate (Aldrich), n-hexyl isocyanate (Kodak), n-octylisocyanate (Kodak), N,N-dimethylformamide and



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toluene were distilled from calcium hydride before use. The N,N-dimethylformamide was stored over molecular sieves. The initiator was prepared from the freshly distilled N,N-dimethylformamide and sodium cyanide as a saturated solution. Undecyl isocyanate was synthesized from lauryl chloride (Aldrich) by the method of Boehmer (14) as described below.

Synthesis of Undecylisocyanate

Into a 2-L round bottom flask fitted with a long condenser and a calcium chloride guard tube, 173mL of lauryl chloride (0.75 mole) was added slowly to 280mL of toluene containing 65g of sodium azide (1.0 mole) already in the flask. The reaction mixture was slowly heated with constant stirring to a point of gently reflux. The reaction mixture was allowed to reflux for about 8h until no further nitrogen was evolved from the reaction product. It was then cooled to room temperature and the solid material was filtered out. The solvent was evaporated and the monomer was purified by vacuum distillation.

Synthesis of Copolymer

Into a 500-mL three-necked round-bottom flask fitted with a mechanical stirrer and serum septa, nitrogen gas was introduced by means of syringe needle. Before adding the monomer and solvent into the reaction flask, the flask was heated with continuous nitrogen gas purge to remove the trace amount of moisture present in the system. Then 50mL of N,N-dimethylformamide, 7.9g of undecylisocyanate (0.04 mole) and 3.4g of propylisocyanate (0.04 mole) were introduced into the reaction flask through a syringe needle. (When the polymerization reaction was tried with 50:50 volume of dimethylformamide and toluene, no polymer precipitated out after the initiator was added.) The reaction mixture was cooled externally using dry ice-acetone bath. When the reaction mixture became solid, the dry

ice-acetone bath was slowly removed in order to stir the contents. As soon as the solid dissolved, the dry ice-acetone bath was introduced once again. This procedure was repeated several times with constant stirring and continuous nitrogen purge. The above process was designed to remove any dissolved oxygen in the reaction mixture. While keeping the reaction mixture just above the melting point of dimethylformamide (-58°C), 2mL of catalyst solution was injected with vigorous stirring. The polymer precipitated immediately from the reaction medium, but was allowed to stand at dry ice-acetone temperature for 5 minutes after the initiator was added. Finally, methanol was added and the polymer was filtered and washed with methanol several times. The polymer was dried in a vacuum oven at 50°C for 3 days.

Preparation of Polymer Films

Thin uniform films of the polymers were cast on glass plates from chloroform solutions. Films, 0.05 to 0.14 mm thick, were dried first at room temperature and finally at 50°C for 2 days in a vacuum oven before mechanical testing.

Characterization

Infrared spectra were taken using films cast from chloroform on NaCl plates in a Nicolet-60SX Fourier transform infrared spectrometer. To improve signal-to-noise, 32 scans were averaged. Background spectra were subtracted from the specimen spectra before recording.

A DuPont model 950 thermal analyzer was employed for thermogravimetric analysis (TGA). A sample of $\sim 20\text{mg}$ was heated at $20^{\circ}\text{C}/\text{min}$ in a nitrogen atmosphere. Differential Scanning Calorimetry (DSC) was performed on a Perkin Elmer DSC-2 attached to a data station and printer. The specimens were heated at a rate of $20^{\circ}\text{C}/\text{min}$ in nitrogen.

Thermal optical analysis measurements were carried out on thin films sandwiched between microscope slides and observed with a polarizing binocular microscope equipped with a stabilized light source, a heated stage and a photodetector on one ocular. The intensity of the light was recorded as a function of temperature. The instrument was calibrated using naphthalene and adipic acid.

The thermal transitions of the undecylisocyanate copolymers were measured with a DuPont model 990 DSC instrument at 20°C in nitrogen. Indium was used for temperature calibration. In most cases a confirming run was performed heating a fresh specimen to 60°C at a heating rate of 20°C/min and quenching down to 110°C using liquid nitrogen. It was then scanned at 20°C/min.

Dynamic mechanical analyses were conducted on cast films with a Rheovibron DDV II viscoelastometer at 11Hz. The temperature was raised by manual control at a rate of $\sim 1^\circ\text{C}/\text{min}$.

Tensile tests were performed on an Instron instrument at 23°C using a strain rate of 100%/min. Test specimens in the form of strips were cut from the dried polymer film samples.

RESULTS AND DISCUSSION

The purity of the undecylisocyanate was confirmed by the complete disappearance of the IR absorption band at $\sim 1800\text{ cm}^{-1}$ and the appearance of a very strong absorption band at $\sim 2275\text{ cm}^{-1}$ corresponding to $-\text{COCl}$ and $-\text{NCO}$ respectively. The composition of the monomers in the feed was 50:50 mole ratio, and was assumed to be the same in the copolymers. The yields of the polymers are given in Table I.

The results of the IR spectral analyses of poly(undecylisocyanate) and copolymers are given in Figure 1 and Table II. The C=O stretching frequency was found to be essentially independent of the copolymer composition. The

IR spectra of poly(undecylisocyanate) reported by Aharoni (6) showed a strong carbonyl doublet (1685 and 1695 cm^{-1}). In contrast, for the same polymer, we observed only one strong absorption band at $\sim 1697 \text{ cm}^{-1}$. The absorption bands at $\sim 1075 \text{ cm}^{-1}$, corresponding to C-N stretching, gradually shifted to higher wave number when the monomer was changed from propyl to octylisocyanate. Similarly it was found that there were noticeable irregular changes occurring in the absorption region between 1160-1390 cm^{-1} corresponding to the disubstituted amide structure (15) and other bands. The strong absorption band observed for poly(undecylisocyanate) at 1101 cm^{-1} was not observed in all the copolymer systems.

The DSC results of poly(undecylisocyanate) and its copolymers are presented in Figures 2 and 3 and in Table III. Scans of the virgin polymer showed, in addition to other transition peaks observed for all the poly(undecylisocyanate) copolymers, an endothermic peak at $\sim 72^\circ\text{C}$ (peak maximum) for poly(undecylisocyanate) and an undecyl/octyl copolymer. However, in the second scan, this endotherm disappeared, while the other transitions were unaffected.

In all the DSC curves, the endothermic transition at $\sim 36^\circ\text{C}$ may be due to the melting of the long aliphatic side chains. That melting of the side chain was not affected by the presence of comonomer in the copolymer, as evidenced from the constant transition temperatures observed for all the homo and copolymers.

Aharoni (10) stated that since thermal decomposition of some polyisocyanates may set in at a temperature significantly lower than the clearing temperature (T_c), the T_c of these polymers may not be observable with DTA or DSC. Though he observed the T_c transitions from DTA-DSC analysis for butyl, hexyl and octylisocyanate homopolymers, he did not observe any T_c for poly(undecylisocyanate) homopolymers. Our DSC results from both types of experiments clearly indicate a clearing transition. This result itself

suggests that the polymer does not undergo decomposition before the melting of the liquid crystal. The clearing transition was observed in all the copolymers as well. The temperature difference between the clearing temperature and decomposition provides a measure of the range of the isotropic state for these polymers. By varying the comonomer from undecyl to propylisocyanate, this difference in temperature (Figure 3) increased from ~20 to 40°C. Thus the introduction of comonomer produces materials with a practical temperature range for studying the isotropic state of these liquid crystalline systems. This improvement is due mainly to a decrease in the clearing temperature of the copolymer (Figure 3).

The clearing points observed from the thermal optical analysis are given in Table III and are found to increase when the comonomer was varied from propylisocyanate to octylisocyanate. With the exception of poly(undecylisocyanate) itself, this increasing trend is in agreement with the T_c observed from the DSC analysis. We do not have an explanation for the discrepancy in the case of the homopolymer. In general, an increase in T_c of the polymer systems can be achieved either by increasing the interaction of the chains, or by increasing the rigidity of the main chain (16,17). Both effects might be achieved by introducing groups which can form intra or intermolecular hydrogen bonds. For acrylate polymers, the observed effect of pendant groups on T_g , which is sensitive to similar factors, is that T_g decreases with increasing length of side chain until the length reaches 8 carbons, and increases after this (18). We would thus expect a decrease of T_c on increasing the alkyl chain length in a series of poly(alkyl isocyanate) homopolymers, and this has indeed been reported (5,6,10). The decrease of T_c on decreasing the alkyl chain length of one half of the side chains of a dodecylisocyanate copolymer is again probably entropic in origin, but in this case the largest contribution being a gain

in entropy of the crystal as the size discrepancy between each comonomer increases. This is commonly observed with the addition of small amounts of foreign comonomer into crystalline polymers; e.g. propylene into polyethylene.

The thermal stabilities of these polymers, as found with TGA analysis, are presented in Figure 4 and Table IV. The initial decomposition of these polyisocyanates was observed to start at $\sim 460^\circ\text{K}$ (190°C) in agreement with the DSC. Moreover the shapes of the curves demonstrated that the rate of decomposition was faster for the copolymer than for the homopolymer, once the process began. An additional feature was a two-stage decomposition. All the polymers underwent complete decomposition at $\sim 450^\circ\text{C}$.

Because many mechanical and physical properties change in the neighborhood of glass transition temperature (T_g), it is very important to determine the T_g of these liquid crystalline polymers. Though Aharoni (6) reported the glass transition temperatures for some of his poly alkylisocyanates, he also mentioned that occasionally observed low-temperature transition temperatures may not be true glass transitions. Howard and coworkers (12) tried to measure the glass transitions of copolymers made from butylisocyanate with ethylisocyanate using dynamic mechanical and DSC analyses. From the dynamic mechanical analyses, they found two peaks in $\tan\delta$, one in the range of -20° to 0°C and another near 100°C . However, they could not observe the glass transition temperatures from DSC analyses and concluded that ΔC_p must be very small and therefore the DSC method could not be used to measure T_g with these poly alkylisocyanates. The results of our T_g analyses are given in Table V and Figure 5. In contrast to the reports of Aharoni or Howard et al., the DSC curves clearly showed the glass transition temperatures of undecylisocyanate copolymers.

From the dynamic mechanical analysis, the Young's modulus and loss factor ($\tan\delta$) were obtained as a function of temperature through the glass transition region. Sample results are given in Figure 6; the peak in $\tan\delta$ is quite distinct. The copolymers all showed one $\tan\delta$ peak in the temperature range -15 to -40°C . The glass transition temperatures ($\tan\delta$ peak) are included in Table V.

The glass transition temperatures obtained from DSC analysis and dynamic mechanical measurements were in reasonable agreement. These values are plotted as a function of the number of carbon atoms (n) present in the comonomer in Figure 7, the homopolymer being the $n=1$ member of the series.

As seen from both analyses, glass transition temperatures of these copolymers decreased first when the comonomer chain length was increased from ethyl to hexyl. After this, the glass transition temperatures increased with further increase in chain length from octyl to undecyl. This behavior may be associated with the increasing hydrocarbon content of the copolymers; this hypothesis was tested by examining reported trends in homologueous series of alkyl-substituted homopolymers. The relevant series examined have as their $n=1$ member the following polymers:

poly (methyl chloroacrylate)

polypropylene

poly (vinyl methyl ether)

poly (methyl acrylate)

poly (methyl methacrylate)

poly (p-methyl styrene)

The T_g 's for these polymers, with up to 13 methylene units in the side chain (m), were obtained from a number of sources, mainly the Polymer

Handbook (18). While the reported Tg's are not without error, the general trend with m is a decrease, followed by an increase. For application of this trend to the polyisocyanate copolymers, the entire set of Tg's was fitted to the following empirical model:

$$1 - \frac{T_g}{T_{g,0}} = m(a_1 + a_2m + a_3m^2 + a_4T_{g,0})$$

with the following values for the constants:

$$a_1 = 0.0723 \pm 0.0199$$

$$a_2 = -0.0126 \pm 0.0045$$

$$a_3 = 0.00044 \pm 0.00026$$

$$a_4 = 0.00010 \pm 0.000047$$

Note that $m=n-1$ and $T_{g,0}$ is the Tg of the $m=0$ ($n=1$) member.

While not providing a perfect fit ($r^2=0.67$, $F=32.7$) it does describe the major trends and was hypothesized to be a good predictor for the expected behavior of the Tg for poly (alkylisocyanates). As the position of Tg of polyundecyl isocyanate ($m=10$) at -15°C was very close to the polyacrylates, a $T_{g,0}$ of 10°C was assumed; this would correspond to poly(methyl isocyanate).

With this in hand the above relationship then provides the Tg's for homopolymers of $m < 10$. To predict the Tg's of 50:50 copolymers, the Fox equation was assumed. While discrepancies from the Fox equation have been described (19) it is not evident how corrections can be made without additional information. The resulting predicted Tg's for the copolymers are depicted by the dotted line in Figure 7. It is clear from the near agreement between the data and the prediction that the known dependence of homopolymer Tg on alkyl side chain length is completely sufficient for explaining the observed minimum. This agreement also provides further support for the hypothesis that the observed transition is, indeed, the primary (glass) transition.

All the stress-strain curves of undecylisocyanate copolymers showed a smooth and moderate curvature with no distinctive features. The stress-strain behavior of poly (undecylisocyanate) was similar to those reported by Aharoni (20) for this polymer. The failure of poly (undecyl + hexyl) isocyanate occurred at a uniquely high strain. Comparing the viscosity (η_{inh}) and strain values of these co-polymers indicates that the strain at failure increases with intrinsic viscosity ($p=0.019$) but is not correlated with copolymer structure. We were unable to confirm the finding of Howard and co-workers (13) that the tensile strength and modulus are inversely dependent on the length of the side chain.

CONCLUSIONS

Liquid crystalline copolymers containing 50:50 mole ratios of undecylisocyanate with propyl, butyl, hexyl, and octylisocyanate were synthesized and characterized. By making copolymers, the temperature range of isotropic state (i.e. range between the clearing and decomposition temperatures) was increased over that for poly (undecylisocyanate). The results from various analyses showed that all the copolymers undergo decomposition at $\sim 180^\circ\text{C}$. The dependence of T_g on alkyl side chain length and copolymer composition was consistent with that for other alkyl-side-chain polymers.

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Table I

Synthesis of Poly(undecylisocyanate) and 50:50 Copolymers

<u>Polymer</u>	<u>Abreviation</u>	<u>Yield %</u>	<u>η_{inh}^a</u>
Poly(undecylisocyanate)	PUDI	79	3.96
Poly(undecylisocyanate-co-ethylisocyanate)	PUDETI		
Poly(undecylisocyanate-co-propylisocyanate)	PUDPRI	67	8.90
Poly(undecylisocyanate-co-butylisocyanate)	PUDBUI	73	4.89
Poly(undecylisocyanate-co-hexylisocyanate)	PUDHYI	66	10.77
Poly(undecylisocyanate-co-octylisocyanate)	PUDOCI	75	3.58

^aInherent viscosity determined in toluene at 25°C with a concentration of 0.1 g/dL.

Table II

Infrared Analysis of Poly(undecylisocyanate) copolymers
Absorption wavenumbers, cm^{-1} , and intensities^a

<u>Polymer</u>	<u>C=O stretch</u>	<u>C-H stretch</u>	<u>C-H Bending</u>	<u>C-N stretch</u>	<u>Disubstituted amide and other bands^b</u>
PUDPRI	1699	2930(0.56) 2860(0.31)	1459(0.21)	1079(0.47)	1207(0.46) 1271(0.22) 1286(0.26) 1347(0.49)
PUDBUI	1699	2925(0.57)	1462(0.25)	1089(0.41)	1194(0.46) 1270(0.25) 1292(0.21) 1347(0.46)
PUDHYI	1698	2924(0.37)	1469(0.19)	1095(0.41)	1180(0.48) 1226(0.24) 1241(0.25) 1285(0.22) 1346(0.48)
PUDOCI	1698	2930(0.45) 2855(0.28)	1470(0.30)	1097(0.41)	1171(0.45) 1227(0.20) 1269(0.20) 1286(0.20) 1346(0.43)
PUDI	1697	2921(0.53) 2851(0.34)	1466(0.33)	1075(0.39)	1168(0.39) 1224(0.20) 1264(0.09) 1286(0.17) 1347(0.39)

^aIntensities relative to C=O stretch are given in parantheses

^bsee Ret. 15 for assignment

Table III

Transition temperatures of poly(undecylisocyanate) copolymers

Polymer	DSC transitions ^a , °C					
	<u>T_{m1}</u>	<u>T_{m2}</u>	<u>T_c</u>	<u>T_d</u>	<u>T_d-T_c</u>	<u>T_c, TOA, °C</u>
PUDPRI	35.7	104.5	137(139)	179	42(40)	172
PUDBUI	35.8	104	142(147)	179	37(32)	175
PUDHYI	36.2	103.8	162(163)	184	21(21)	182
PUDOCI	36.0	b	153(161)	189	35(26)	185
PUDI	35.8	104	155(163) ^c	183	28(20) ^c	170

a T_{m1} = lower melting transition; T_{m2} = solid to liquid crystalline transition; T_c = liquid crystalline² to isotropic transition; T_d = decomposition temperature.

b Not observed.

c Corrected for molecular weight. The corrections were based on the assumption that the concentration of the solutions was dilute enough to assume $n_{inh} = [\eta]$ and that the MW dependence of T_c followed that of PHIC reported by W.R. Krigbaum et al., *Macromolecules*, 18, 973 (1985).

Table IV

Thermogravimetric analysis of poly(undecylisocyanate) copolymers

Polymer	Initial decomposition	Temperatures, °C, corresponding to	
		<u>25% weight loss</u>	<u>>98% weight loss</u>
PUDPRI	190	250	440
PUDBUI	190	250	370
PUDHYI	195	270	380
PUDOCI	190	300	430
PUDI	195	310	450

Table V

Glass transition temperatures observed for
poly(undecylisocyanate) and copolymers

<u>Polymer</u>	<u>DSC (°C)</u>	<u>Rheovibron (°C)</u>
PUDI	-16.5	-14.0
PUDETI	-32.1	-25.0
PUDPRI	-34.0	-32.0
PUDBUI	-39.5	-40.0
PUDHYI	-43.1	-40.0
PUDOCI	-36.7	-24.0

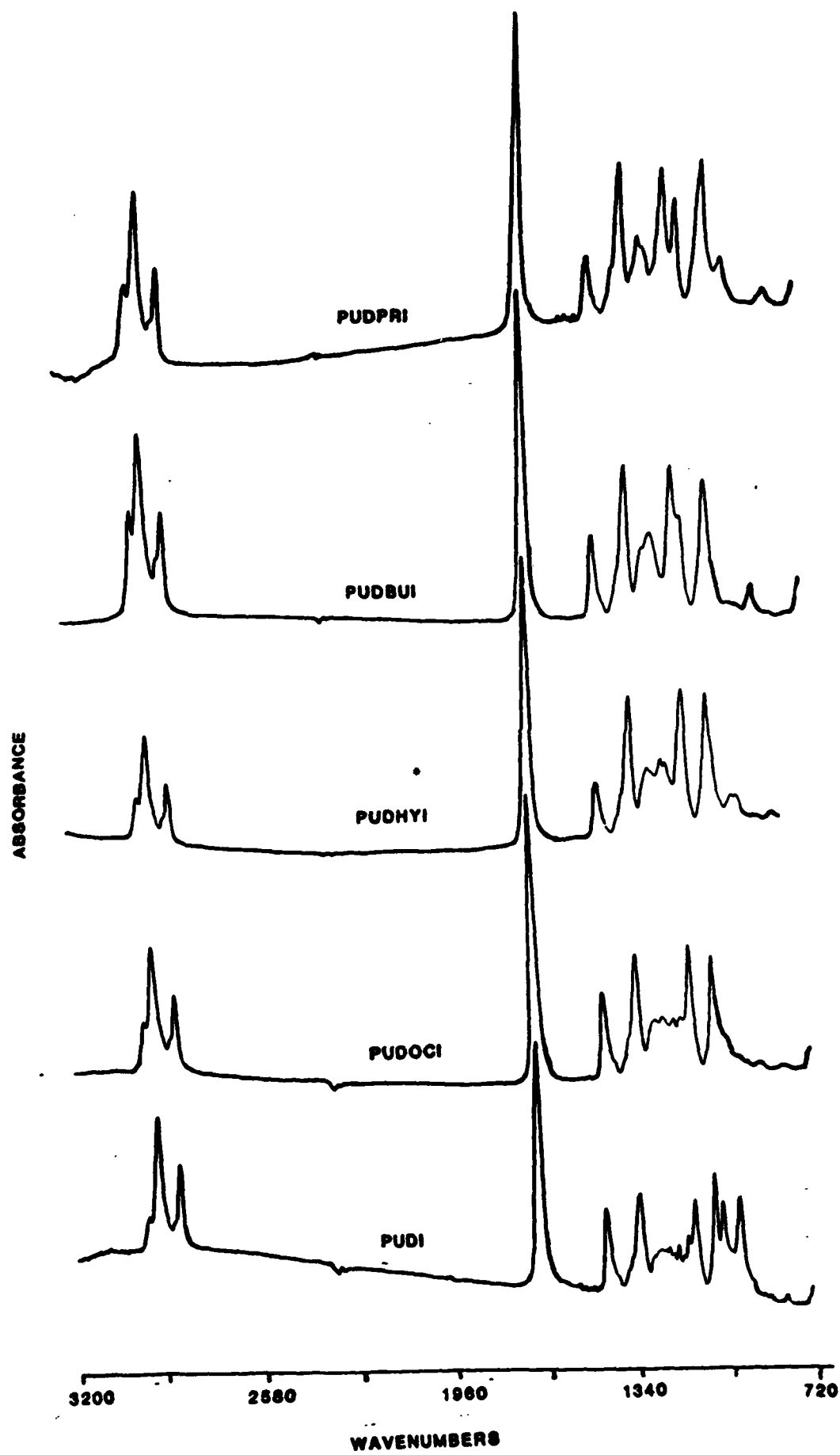


Fig. 2
FIG 2

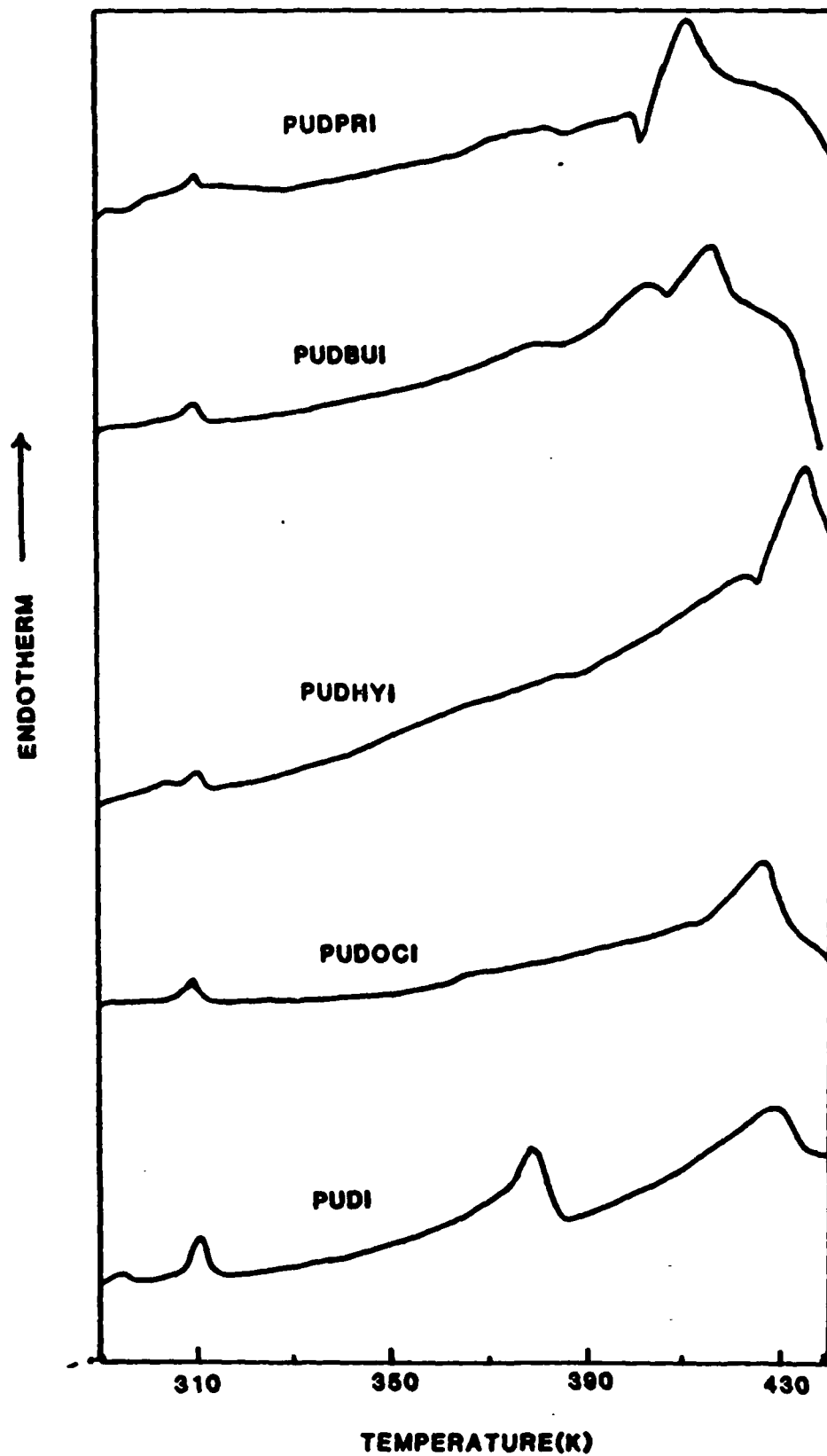
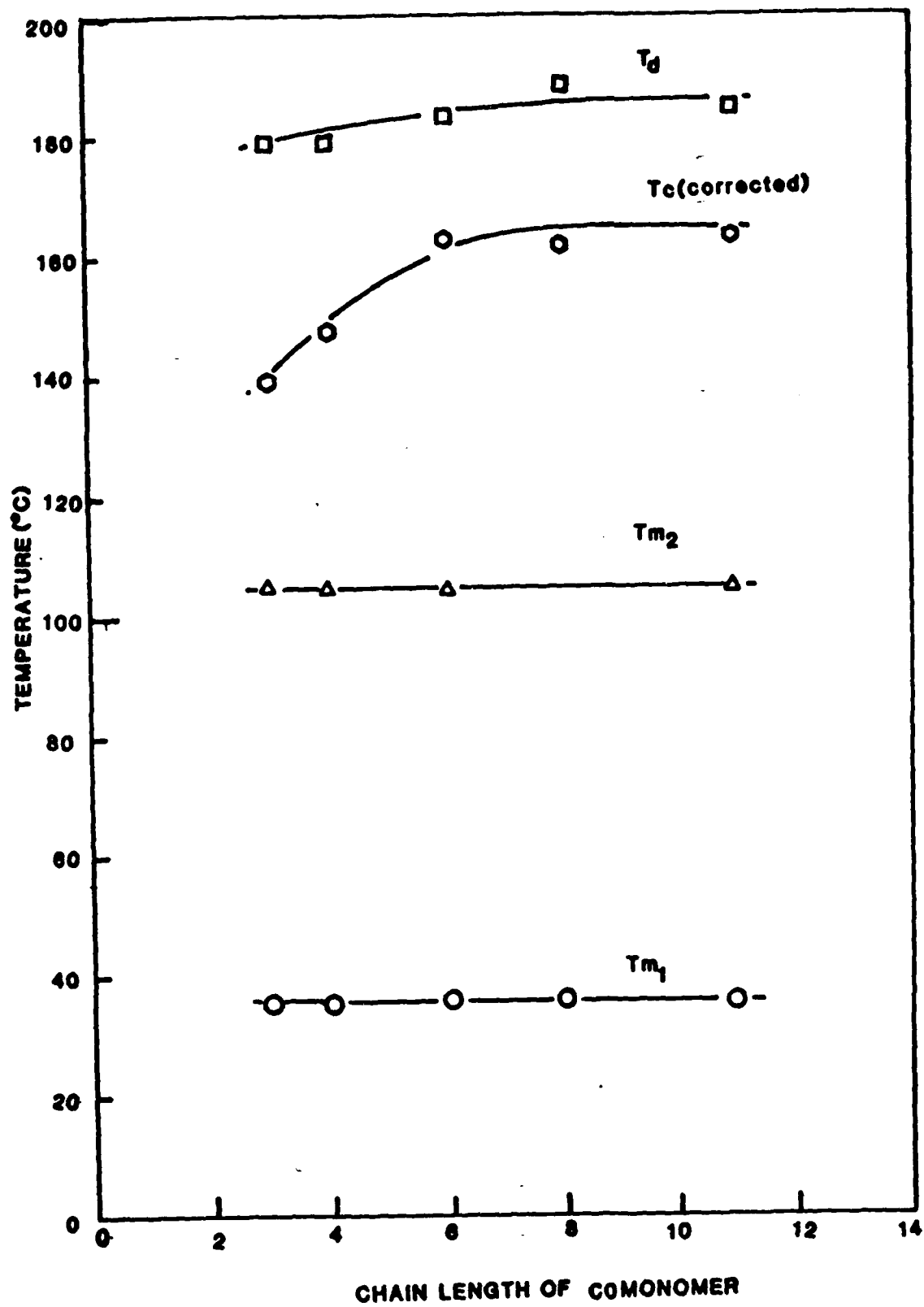
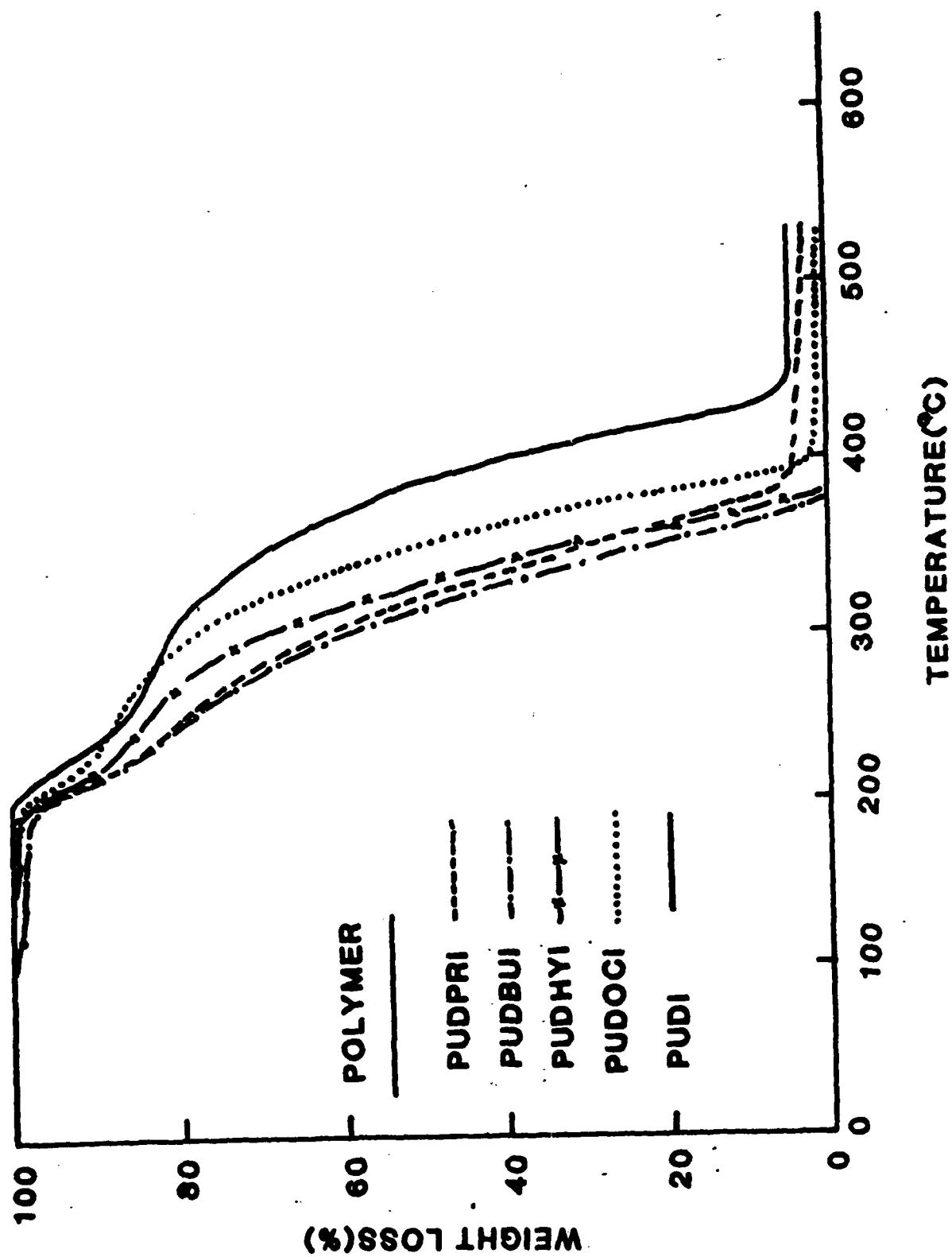


Fig 3

Fig 3





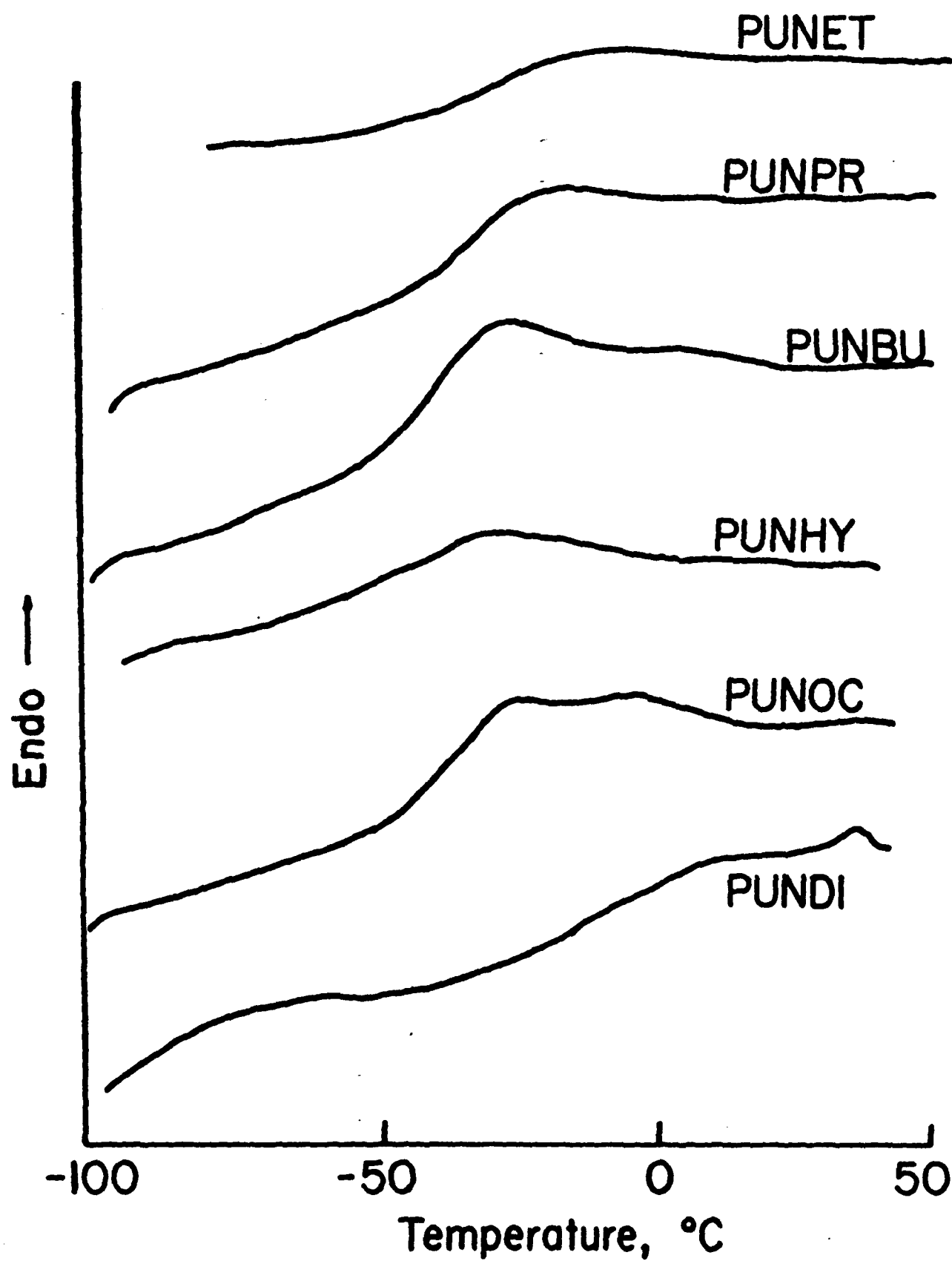


Fig. 6

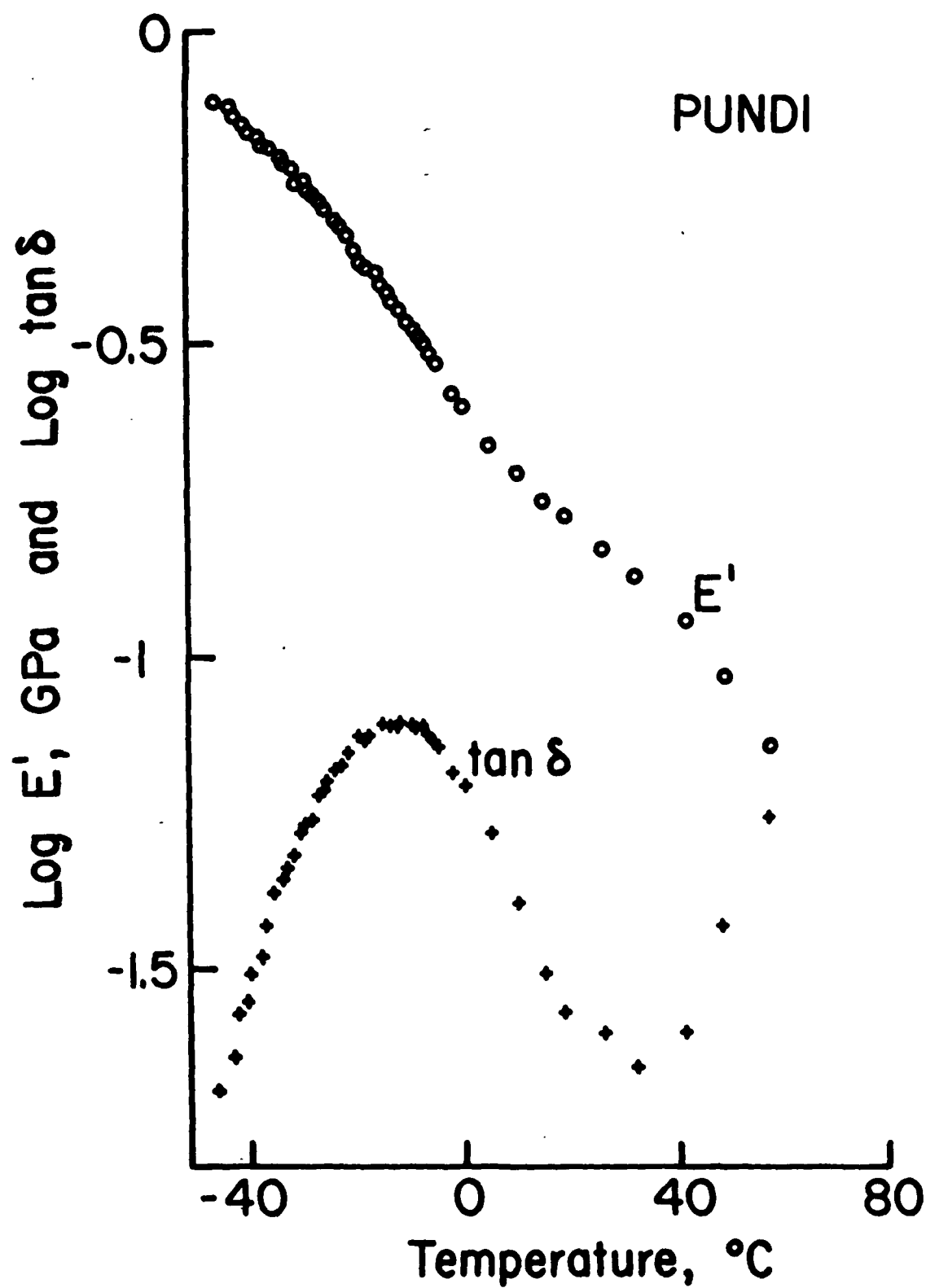
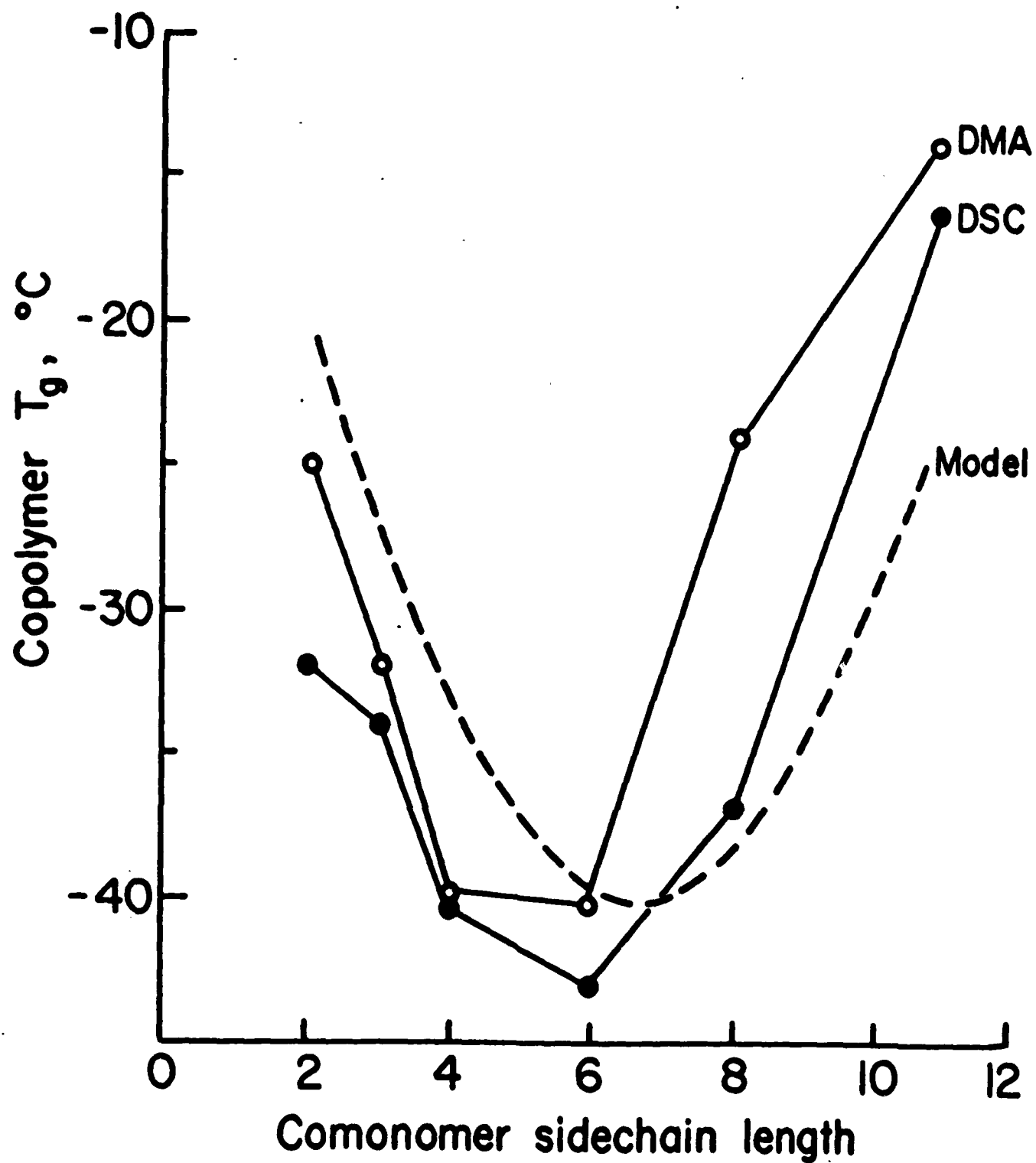


Fig 7



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