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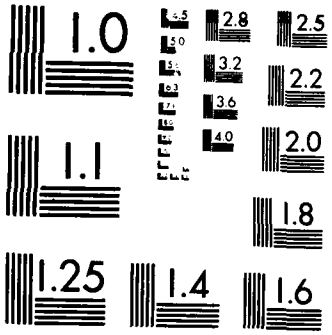

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VARIABLE TEMPERATURE SOLID STATE NMR OF SIDE-CHAIN CRYSTALLINE COMB POLYMERS

by

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Several comb polymers containing C_{16}-C_{18} side-chains were examined by variable temperature ^{13}C CP/MAS NMR. Polymers with backbone glass transition temperatures below room temperature displayed high degrees of side-chain crystallinity as evidenced by internal CH_2 group chemical shifts of ca 33.2 ppm, comparable to the value displayed by all-trans CH_2 segments in the crystalline domains of polyethylene. Above the side-chain melting points, this peak shifts to ca 30.7 where the peak of molten polyethylene is found. On cooling, the side-chains of these polymers rapidly recrystallize. The alternating copolymer of maleic anhydride and 1-octadecene is not capable of side-chain crystallinity even at -40°C because of greater distance between pendent groups and a backbone Tg greater than room temperature. The octadecanamide derivative of poly(dehdroalanine methyl ester) possesses a backbone Tg above room temperature and shows good side-chain crystallinity in precipitated materials. Once melted and cooled, however, recrystallization is greatly restricted by the backbone rigidity. Solid state NMR thus provides a sensitive tool for studying the side-chain crystallinity in relationship to backbone Tg's and thermal history.

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Variable Temperature Solid State NMR of Side-chain Crystalline Comb Polymers

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Polymers with side-chain groups capable of crystallization independent of the backbone have been of interest for many years. Recent reviews summarize the syntheses and characterization of a large number of different families of comb polymers[1,2]. The easiest to synthesize and evaluate with respect to property trends in a homologous series are those containing linear alkyl side-chains. Derivatives with greater than 8-12 carbons form side-chain crystals with hexagonal packing of the alkyl moieties. In this type of packing, individual alkyl groups adopt an all-trans conformation but with rotational disorder between side-chains[2].

We recently became interested in derivatives of dehydroalanine (DHA) because of the multiple functionality available in the parent monomer. A wide variety of carboxylic acid and amine derivatives can readily be incorporated before generation of the reactive vinyl group. Radical polymerization of dehydroalanines is rapid, often takes place spontaneously, and usually occurs with good conversion[3]. We have synthesized a series of alkylamide derivatives[4], and shown that the C_{18} monomer forms monolayers capable of in situ photopolymerization to stabilized polymeric monolayers[5].

In the process of characterizing the various DHA polymers synthesized, we became interested in the use of solid state ^{13}C NMR to evaluate several thermal transitions that we have tentatively ascribed to separate side-chain and backbone molecular relaxation processes. In the course of this project, a closely related paper appeared on the use of variable temperature CP/MAS to study side-chain and backbone motion of poly(γ-n-octadecyl L-glutamate) (POG)[6]. We describe here the variable temperature ^{13}C CP/MAS NMR behavior of the C_{18} DHA polymer along with several commercially available comb polymers for comparison.

Experimental

The C_{18} DHA was synthesized as previously described[3-5]. Other comb polymers were purchased or obtained as evaluation samples from various sources. Thermal transitions were determined on a DuPont 910 DSC and 9900 data station, and on a Leitz polarizing microscope equipped with a Mettler hot stage. Solid state ^{13}C NMR was carried out at 50.32 MHz on a Bruker MSL-200 equipped with a Bruker multinuclear CP/MAS probe.

For each spectrum, several hundred to several thousand acquisitions were collected with 5 millisec contact times and 3 sec delays between pulses.

Results and Discussion

The polymers chosen for study all possess C_{16} or C_{18} pendent groups, but vary in side-chain melting point (T*m) and backbone Tg. Polymer 1 possesses a Tg well below -100°C and the highest T*m (42°C). At the other extreme is polymer 4 with a Tg of 87° and a T^*_m of -13°. The Tg's of 2 and 3 are well below the NMR analysis temperatures while that of 5 is 81°. The T*m's of these three polymers are 40°, 32° and 35°, respectively. It is informative to compare the solid state ^{13}C NMR spectra of these polymers with each other at temperatures above and below their T*m values.

Figure 1 gives spectra (from a to e) for polymer 3 in the as-obtained, highly crystalline state; at 42°C, just above the temperature for complete melting of the side-chains; at the beginning of cooling and recrystallization; after 3 h at 27°C; and the difference spectrum in which trace d was subtracted from trace c. It is clear that major changes in the chemical shifts and peak widths of the side-chain carbons occur. In the initial spectrum (a), the peak at 33.2 δ corresponds to interior methylene groups in hexagonal crystalline packing in which the polymethylene chains are fully extended in the trans conformations but with no registry of adjacent chains. This is analogous to the peak observed in polyethylene[7] and in the POG octadecyl-substituted polypeptide[6]. Hexagonal packing of linear alkanes is usually called the "free rotor" form since the chains seem to exhibit no common rotational alignment. These side-chains may exist in crystalline domains as well as in more mobile regions as long as the polymethylene units maintain the all-trans conformation.

Trace b was taken at a temperature above both Tg and T*m; that is, both backbone segmental motion and side-chain "liquid" motion are present. Cross polarization efficiency is low and greatly increased acquisition times were required to obtain good signal-to-noise. Peaks are sharp with chemical shift values for the side-chain carbons corresponding to those of melted alkanes and molten polyethylene. During cooling and recrystallization of the side-chains (traces c and d), the characteristic peaks for the internal all-trans methylenes at 33.2 δ and the penultimate CH_2 at 25.0 δ reappear. The same behavior was observed for POG[6], and for polymers 1-3 and 5 (see the Table). The (trace d - a fraction of trace c) difference spectrum (e in Figure 1) gives the peaks for amorphous side-chains coexisting with crystalline regions during side-chain crystallization. Narrow peak widths and chemical shift values similar to the molten values (trace b) support this assignment. This method allows the direct observation of

both regions of the bulk polymer and should be usable for qualitative characterization and evaluation of the kinetics of side-chain crystallization.

Table 1. Side-chain chemical shifts for polymers 1-5[a].

Polymer	Internal CH_2's[b]		γ-CH_2	β-CH_2	α-CH_3
1	33.3	----	----	24.9	15.3
1 melt	----	30.6	33.6	23.4	14.8
2	33.3	----	----	25.0	14.7
3	33.2	30.9	----	25.0	14.9
3 melt	----	30.6	32.7	23.4	14.7
3 c - d	----	30.7	32.7	23.5	14.8
4	----	30.6	32.7	23.4	14.7
4 -40°	32 broad		----	23.3	14.9
5	33.1	30.9	----	24.9/23.8	14.7
5 melt	----	30.5	32.5	23.2	14.5

[a]Peak assignments are the same as in reference 6.

[b]For internal CH_2's: the first entry is for crystalline trans units, the second for amorphous or melted CH_2 groups.

Figure 2 gives the spectrum for polymer 1; that of polymer 2 is very similar except for backbone peaks. With the high degree of backbone flexibility for these polymers, side-chain crystallization is very favorable, giving materials with excellent peak sharpness and chemical shifts consistent with hexagonal packing[6,7]. In contrast is the spectrum of polymer 4 (trace a, Figure 2). At 27°C, side-chain melting has occurred yet the polymer is well below its Tg and the backbone is rigid. This leads to the novel situation of having a "glassy" polymer backbone suspended in a sea of molten side-chains. The chemical shifts correlate very well with those of side-chain melted 1-3. On cooling to below the apparent T*m, the peaks broaden and move downfield but do not reach the values of highly crystalline side-chain polymers. No peak corresponding to a side-chain crystalline domain is observed despite DSC evidence of a melting transition on temperature increase. A referee has suggested that this peak broadening may be due to molecular motion interfering with proton decoupling in noncrystalline regions. It is clear that because the pendent groups on polymer 4 have two more atoms per repeat unit than the other comb polymers examined, they cannot pack as easily in side-chain crystallites.

Polymer **5** displays some features common to **1-4** along with a unique property related to a separate relaxation process observed in this polymer at ca. 70-85°C. Figure 3 gives spectra of polymer **5** under several conditions. Trace **a** corresponds to the polymer obtained after reprecipitation and standing for months. A high degree of side-chain crystallinity is evident by the greater intensity of the peak at 33.1 δ compared to the amorphous peak at 30.9 δ. Raising the temperature above the T*m value to 323K causes disappearance of the 33.1 δ peak and a sharpening of the amorphous peak which also shifts to 30.5 δ. Additional small changes in the chemical shifts of the side-chain carbons are consistent with those observed previously by others[6]. Temperature induced shifts in the backbone peaks were also seen as shown in Table 2.

Table 2. Side-chain and backbone chemical shifts for polymer 5.

Temp (in K)	C=O's	backbone carbons	CH_3-O	internal CH_2's	penultimate CH_2	terminal CH_3
300	172.3	76.9 60.2	52.9	33.1/30.9	24.6/23.8	14.7
323	172.5	75 60.5	52.8	32.5[a]/30.5	25.3[a]/23.1	14.5
353	172.6	weak 60.5	52.4	32.4[a]/30.3	25.5[a]/23.1	14.4
300(cooled)	172.5	75 60.0	53.0	32.6[a]/30.6	25.0[a]/23.3	14.6

[a]New peaks normally hidden by peaks in row 1 at 33.1 and 24.6 δ.

Raising the temperature to 353K, the temperature at which a second thermal transition is observed in the DSC of this polymer, causes further sharpening of the side-chain internal CH_2 peak with broadening and decreased intensity for the other side-chain and backbone peaks (Figure 3b). This is consistent with increased motion and flexibility due to molecular relaxation of pendent ester and/or amide moieties. We believe this relaxation involves breaking of amide hydrogen bonds to other amide and/or ester groups along the polymer backbone. Cooling the sample back to 300K (Figure 3c) locks the side-chains into amorphous conformations which crystallize very slowly compared to the other comb polymers studied. Inter- and especially intramolecular hydrogen bonding may restrict molecular motion so that reorganization into crystalline lattices is reduced.

Conclusions

Variable temperature ^{13}C CP/MAS offers a sensitive tool for examining side-chain crystallinity in comb polymers. More importantly, it offers a unique tool for simultaneously observing both ordered and disordered states of the side-chains including completely melted and liquid-like states coexisting with crystalline domains.

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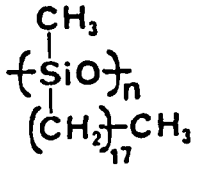

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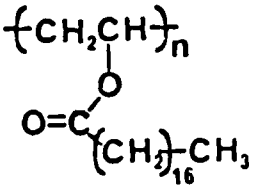

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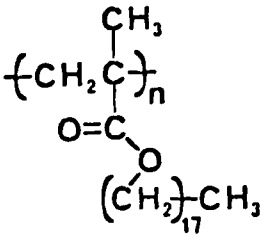

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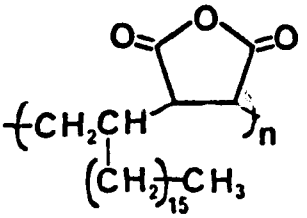

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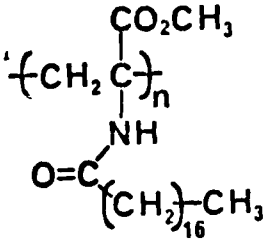

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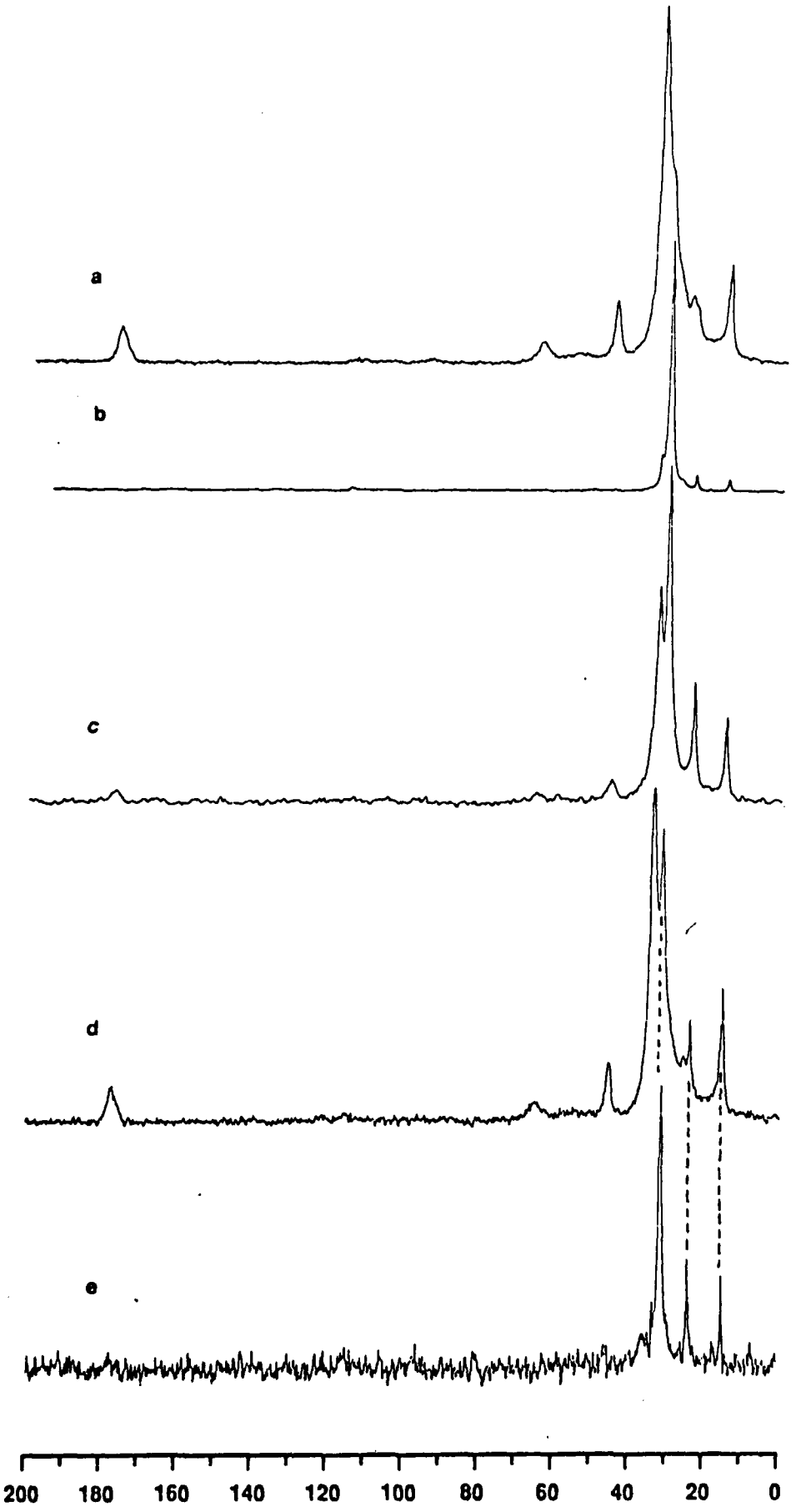

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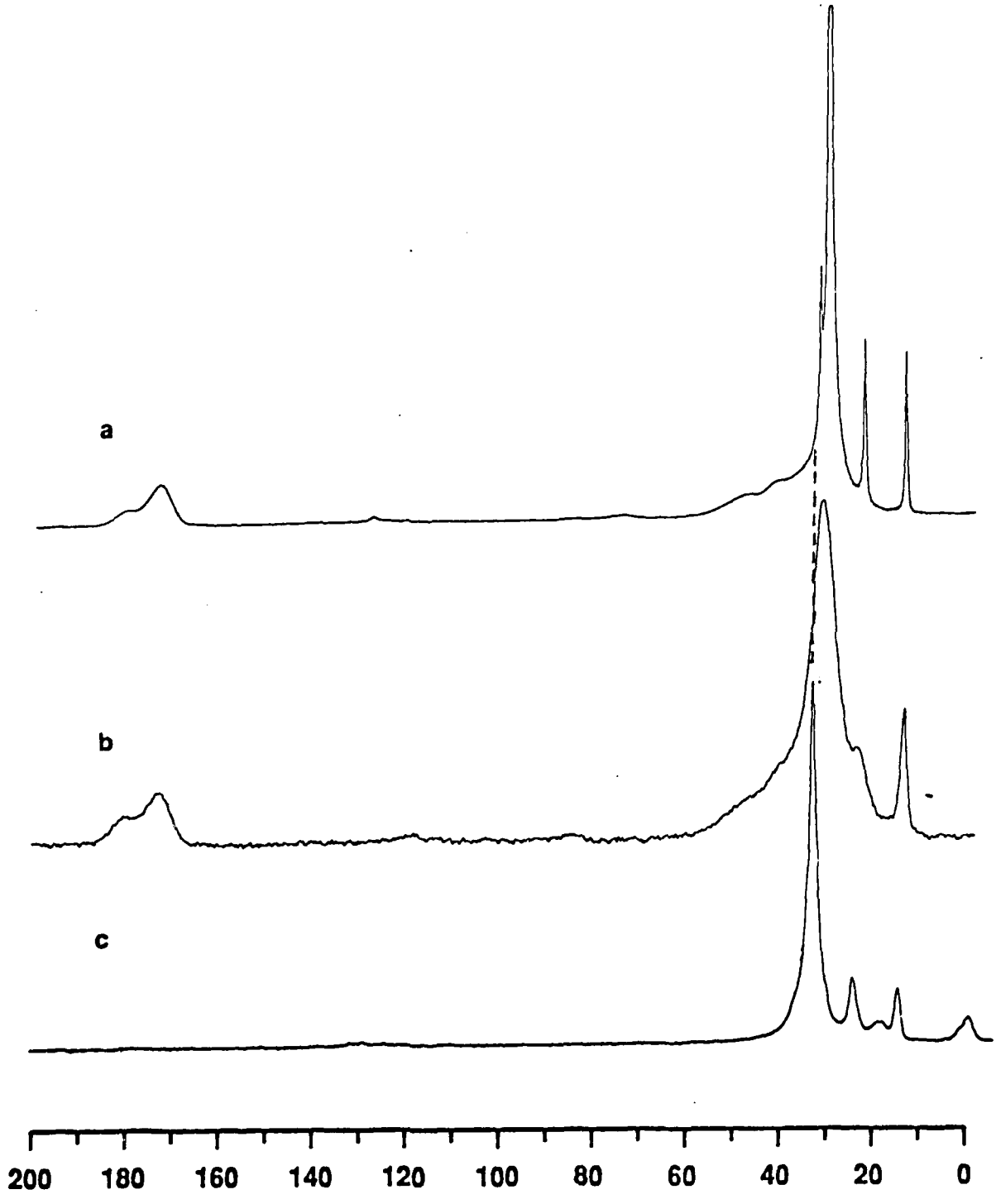

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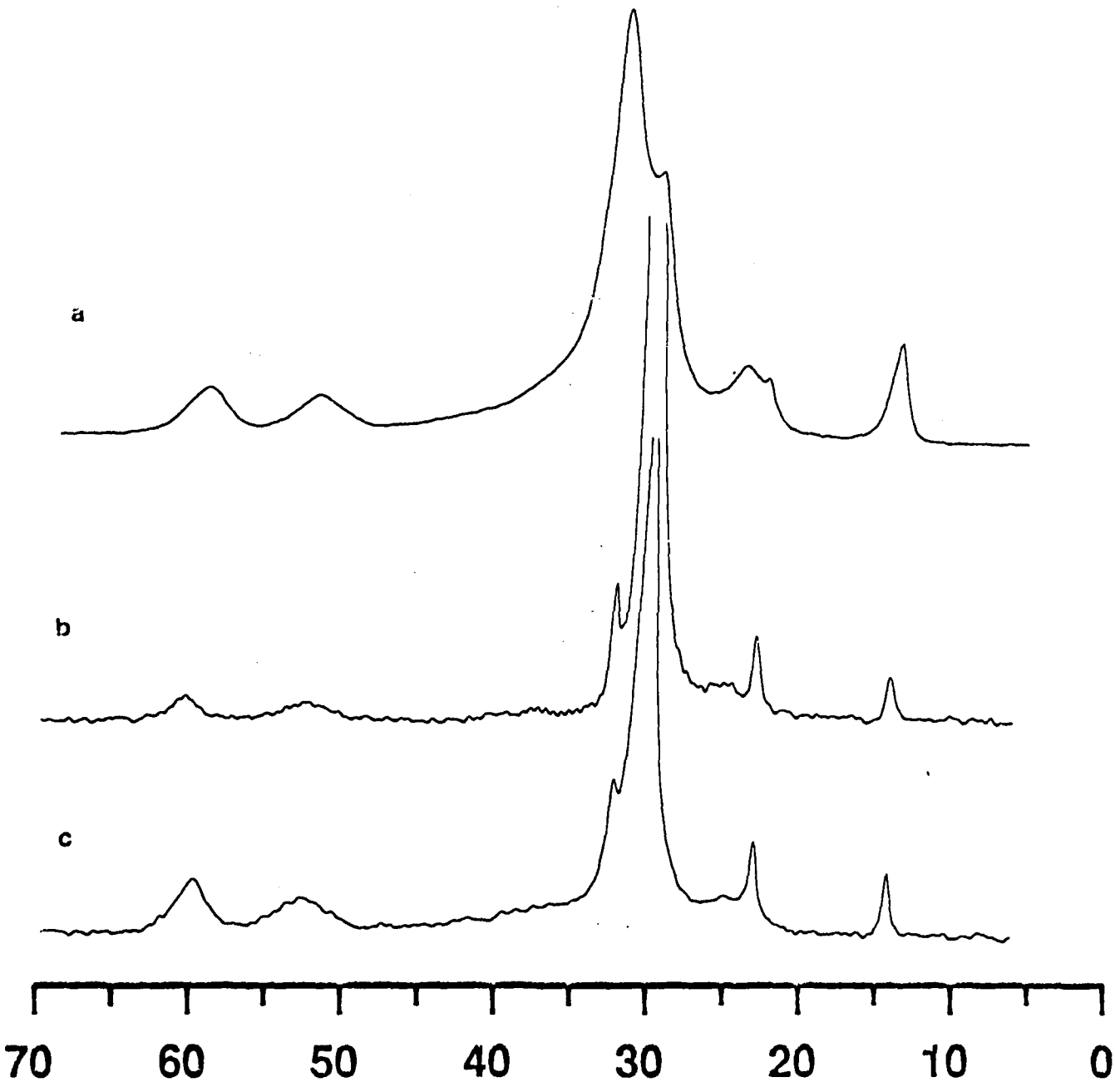

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