

Solid state reactivity of a series of bis(carboxylic acid) esters of 2,4-hexadiyne-1,6-diol

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To achieve an insight into the systematic effect of changes in end-groups on the polymerization of disubstituted diacetylenes, a series of closely related bis(carboxylic acid) esters of 2,4-hexadiyne-1,6-diol have been synthesized and their thermal and photochemical polymerization studied. Quantitative conversion measurements show that the reactivity rises rapidly as the length of the paraffinic side group increases, reaches a maximum value for the bis(capric acid) ester and then falls steadily, to almost no reaction, for the highest member of the series. Optical and Raman spectroscopy show that at low conversion freshly formed polymer is in equilibrium with the monomer lattice but segregation of the polymer occurs at higher conversion and on annealing at room temperature. This behaviour can be explained in terms of the molecular packing, which is discussed in terms of molecular models.

INTRODUCTION

Disubstituted diacetylene monomers are capable of producing highly perfect crystalline conjugated polymers by solid-state polymerization, initiation being brought about by heat, pressure light or high-energy radiation, depending on the reactivity of the particular monomer¹. The basic reaction scheme, which is topochemical in nature, is shown schematically in *Figure 1*. The value of the end-group R of the monomer is particularly important, as not all disubstituted diacetylenes polymerize in the solid state and, even if reaction does occur, it need not necessarily proceed to completion or give an ordered single crystal product. As a general rule, solid state polymerization will only occur if the distance between the reacting carbon atoms in the monomer crystal, a_1 in *Figure 1*, is less than 4.0 Å. This separation is determined by the packing of the monomer units which is strongly influenced by the side groups. The optimum packing for topochemical polymerization occurs when $\gamma_1 \sim 45^\circ$ and s_1 is between 3.4 and 4.0 Å^{2,3}. If during this polymerization process, a solid solution of extended chain polymer within the monomer lattice is established, the single crystal character of the monomer is retained. This will occur if the monomer-polymer interfacial energy is low; high values lead to a build-up of strain in the lattice resulting in a limiting conversion or segregation of polymer and monomer and a disordered final product². The end-groups R play an important role here too since the polymer-monomer interaction occurs principally through these groups.

The most thoroughly investigated polydiacetylene is the poly[bis(*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol], where R is $-\text{CH}_2-\text{SO}_3-\text{C}_6\text{H}_4-\text{CH}_3$ and a considerable amount of data already exists for this material⁴⁻⁶. Recent studies of materials closely related to this compound show that small changes in side group structure have dramatic effects on reactivity⁷⁻¹⁰. X-ray structural analyses show that these result from the occurrence of several different conform-

mations of the end-groups of the monomer units and consequent changes in the molecular packing in the solid state. Such changes are due to the interplay of intra- and intermolecular forces and, though progress is possible in understanding these interactions, the complexity of the end-groups makes this difficult. We have therefore turned our attention to simpler end-groups, comprising principally paraffinic chains, for which the interactions are well known¹¹ and which can adopt different conformations. In the present study we have investigated the series of bis(carboxylic acid) esters of 2,4-hexadiyne-1,6-diol, $[\text{CH}_3(\text{CH}_2)_n\text{CO}_2\cdot\text{C}\equiv\text{C}]_2$,

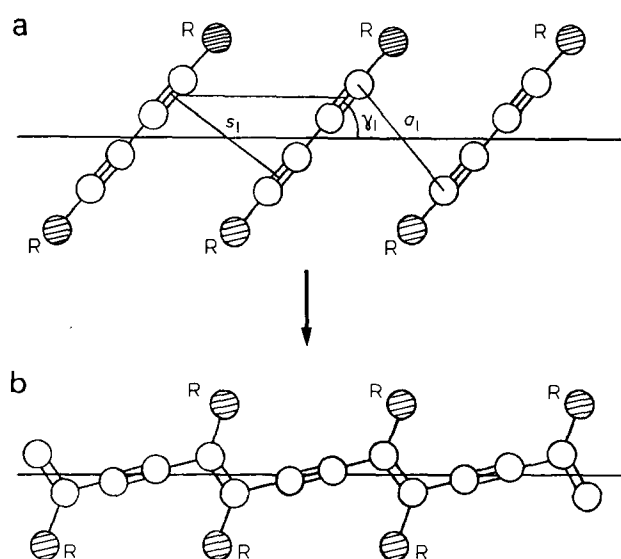


Figure 1 Topochemical solid-state polymerization of diacetylenes showing packing requirements. (a) Stacking of diacetylene monomers in a reactive crystal; (b) diacetylene polymer chain. R represents the end groups in the monomer and side groups in the polymer

Table 1 Bis(carboxylic acid) esters of 2,4-hexadiyne-1,6-diol, $[\text{CH}_3(\text{CH}_2)_n\text{CO}_2\text{CH}_2\text{C}\equiv\text{C}]_2$. Analytical data

Acid derivative	<i>n</i>	Abbreviation	Melting point (°C)		Elemental analysis (%)				Reference
			Found	Literature	Calculated		Found		
					C	H	C	H	
Caproic	4	BCO	28–30*	†	70.58	8.49	70.96	9.37	14
Caprylic	6	BCY	28–32*	26–27	72.93	9.39	71.86	10.55	14
Capric	8	BCI	46	41–45	74.64	10.04	74.79	10.34	14
Lauric	10	BL	55–56	51–52	75.94	10.54	76.03	10.79	14
Myristic	12	BM	59–60	62–65	76.98	10.94	76.52	11.51	14
Palmitic	14	BP	67–68	69–72	77.81	11.26	77.61	12.31	14
Stearic	16	BS	72–74	78	78.44	11.59	77.81	11.91	15

* Some sublimation/decomposition apparent

† Liquid at room temperature

with even values of *n*, ranging from 4 to 16, in order to correlate the solid-state reactivity of the monomers with the systematic change in the length of the paraffinic side group.

EXPERIMENTAL

Physical measurements

Optical absorption spectra were recorded for sample temperatures in the range 80 to 300K using a Cary 14 spectrophotometer. Raman spectra were recorded at room temperature with a coherent radiation dye laser and Spex double monochromator with a photon counting detection system. Laser power levels were less than 10 mW at the sample; this was adequate for a resolution of 4 cm^{-1} , which was less than the observed line width and too low to damage the sample. Melting points were determined by the use of a Dupont Thermal Analyzer (Model 900).

Materials

Commercially available propargyl alcohol, Purum grade (Fluka AG), cuprous chloride, Analar grade (Hopkin and Williams) and dicyclohexylcarbodiimide (DCC), Synchemica grade (Hopkin and Williams) were used without further purification. The monocarboxylic acids, Biochemical Reagent grade (BDH) were further purified by recrystallization from ether.

General synthesis scheme

All the monomers were prepared according to the general procedure outlined below.

(i) 2,4-Hexadiyne-1,6-diol was prepared by the oxidative coupling of propargyl alcohol in an alkaline solution containing Cu^+ ions and purified by recrystallization from toluene¹².

(ii) The esters were prepared by the dehydrative condensation of the respective acids with the diacetylene diol using DCC¹³. To a solution of acid (0.05 mol) and diol (0.025 mol) in dry ether (200 ml) at room temperature, DCC (0.05 mol) in dry ether (100 ml) was added dropwise over a period of 5 min. After a short while, dicyclohexyl urea began to separate from the solution. After stirring for 6 h at room temperature, the urea was filtered off, the filtrate was treated with acetic acid to decompose any excess DCC and was then evaporated to dryness in vacuum. The residue was then redissolved in ether, washed successively with water, dilute sodium bicarbonate solution and water and finally dried over sodium sulphate. The ether was removed *in vacuo* and the product purified by repeated recrystallization from ethanol. In all cases, the esters were white or colourless,

translucent, flake-like, crystalline powders, which coloured to different degrees on exposure to daylight. In all cases, the esters showed clean, well defined melting points and satisfactory elemental analyses. Details of these are shown in Table 1.

Polymerization procedures

Thermal polymerization was carried out by annealing the monomers, at elevated temperatures below the melting point, in the dark, either in a vacuum or an inert atmosphere. Photopolymerization was achieved by irradiation with a low pressure mercury lamp; the finely powdered, freshly recrystallized monomers were suspended in water in a beaker surrounded by water at room temperature and the surface of the well-stirred suspension was irradiated directly, the lamp being kept at a set distance of 2 cm from the water surface. For all samples, conversion to polymer was determined gravimetrically by extraction of the unreacted monomer with acetone, the polymers being completely insoluble in common solvents.

RESULTS AND DISCUSSION

Reactivity of members of the series of esters

Large differences were found in the rates of thermal and u.v. polymerization of these monomers. The rate of thermal polymerization was very slow, measurable conversion to polymer being obtained only for the bis(caprate ester) (BCI) and bis(laurate ester) (BL), for which 1–2% conversion to polymer was achieved after several days annealing.

However, on brief exposure to u.v. irradiation, most of the monomers coloured indicating a much greater polymerization rate. These preliminary experiments indicated that BCI was the most active monomer of the series. Quantitative conversion data was therefore obtained for BCI using exposures to u.v. irradiation of between 1 min and 17 h. The results are shown in Table 2. To assess the relative reactivity of the other members of the series, conversions to polymer were determined for a single value of the irradiation time of 30 min. The results are shown in Table 3. These results show that the reactivity of these monomers rises rapidly from zero for the bis(caproate ester) (BCO) to a maximum for BCI, and then falls steadily for the remainder of the series. It is seen that in the case of BCI, the conversion tends towards a limiting value of approximately 50% polymer. It should be noted, however, that this figure is not an absolute value since, because of the nature of the photopolymerization experiment the polymerization is not completely homogeneous.

Table 2 Percentage conversion to polymer as a function of time for the bis(caprate ester) (BCI). U.v. photopolymerization

Time (min)	Polymer content (%)
0	0.34
1	9.52
5	17.17
15	25.16
30	31.98
60	37.12
120	41.40
1020	48.12

Table 3 Comparative percentage conversions to polymer for the series of esters $[\text{CH}_3(\text{CH}_2)_n\text{CO}_2\text{C}\equiv\text{C}]_2$. U.v. photopolymerization. Single irradiation time of 30 min

Sample (n)	Polymer content (%)
4	0
6	1.03
8	31.98
10	26.32
12	19.80
14	17.32
16	5.56

The small penetration depth of the active u.v. irradiation, of the order 10^{-4} to 10^{-5} cm $^{-1}$, prevents uniform polymerization even for finely powdered crystals. Absorption by the newly formed polymer on the crystal surface prevents the longer wavelength, weakly active but more penetrating, u.v. irradiation from polymerizing the interior during long exposures. These effects typically limit u.v. polymerization of powders to about 80% polymer content¹⁶. This is larger than the value obtained for BCI which suggests that the limiting conversion reflects a strain build up in the polymerizing crystal due to mismatch between polymer and monomer lattices. The crystal cannot lower its energy by further polymerization but it can do so if the polymer segregates from the matrix². This idea receives support from visual observation of the sample which showed that crystallinity was being lost at a conversion greater than 30%. At lower conversions the crystals were bright yellow or golden orange in colour with a distinct metallic sheen, but on further polymerization the samples began to lose their lustre, becoming dull brown and matted in appearance. Similar observations have been reported for the thermal and radiation polymerization of 2,4-hexadiene-1,6-diol^{17,18}.

Optical and Raman spectroscopy

Optical and Raman spectroscopic studies of these materials also indicate that segregation occurs. In the case of BCI, after a short period of u.v. irradiation the now bright yellow crystals show a broad but distinct optical spectrum. On annealing the crystals at room temperature, the corresponding spectrum shows a distinct shift in the absorption edge, as can be seen in *Figure 2a*. On cooling the sample, the original peak shows a distinct temperature dependence and the new absorption is almost temperature independent (*Figure 2b*). Similar results are observed after longer periods of u.v. irradiation without subsequent annealing. This behaviour is characteristic for the π electron spectrum of polymer in a monomer matrix and fully converted polymer or polymer separated from the matrix¹⁹. A similar but more dramatic effect is observed on extracting the insoluble polymer from the monomer crystal matrix. The initial yellow

colour of the polymer in the crystal changes on extraction to a bright red colour which is characteristic of insoluble polymer residues obtained from other partly polymerized diacetylenes²⁰. The absorption edge for the extracted polymer occurs at 600 nm (*Figure 3*). This is somewhat lower in energy than the edge observed in the annealed crystal (see *Figure 2*) and suggests that in the latter case, although the polymer has segregated from the monomer lattice, it has not adopted a relaxed conformation. The less ordered nature of the polymer extract is shown by the much greater width of the absorption edge relative to that for the polymer in the crystal matrix (compare *Figures 2* and *3*).

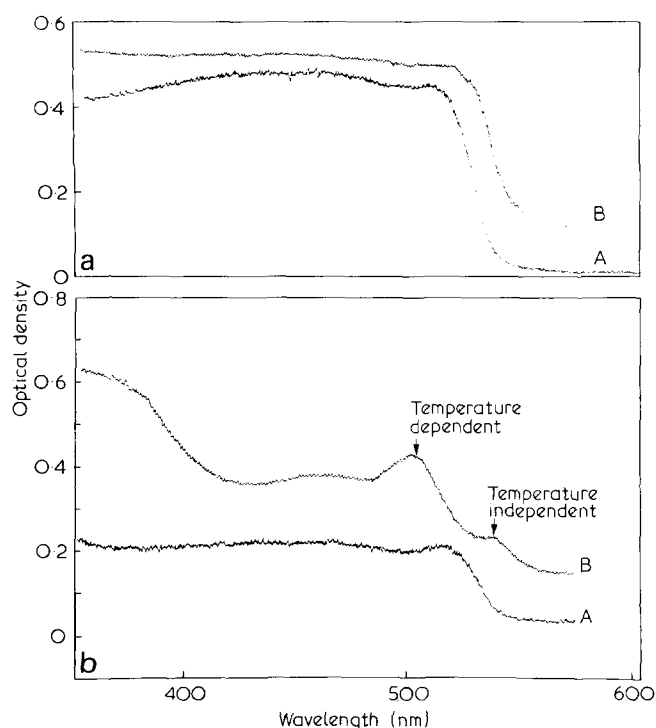


Figure 2 (a) Room temperature optical spectra of BCI. A, U.v. irradiated; (B) u.v. irradiated and annealed at room temperature. (b) Optical spectra of u.v. irradiated BCI showing temperature dependence. A, 300K; B, 100K

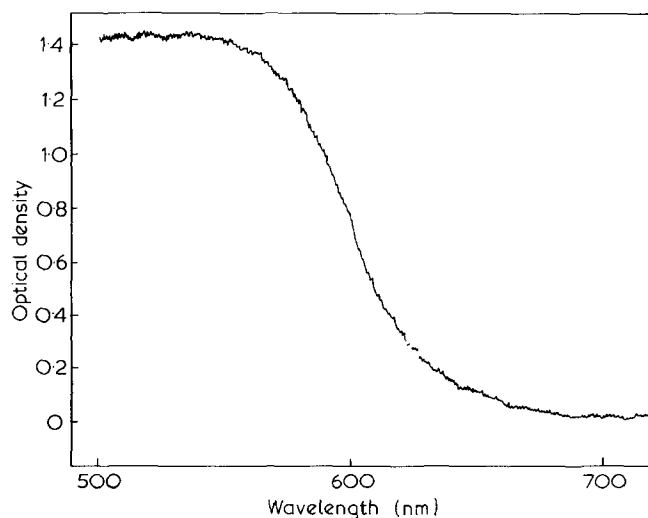


Figure 3 Room temperature optical absorption edge of polymer residue of BCI

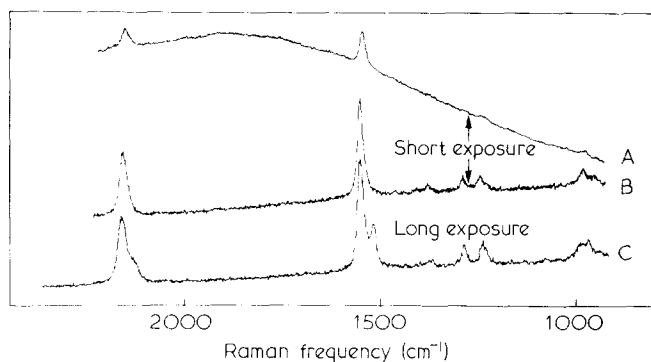


Figure 4 Resonant Raman spectra of u.v. irradiated BCl crystals (i) Short exposure; laser frequency $19\,433\text{ cm}^{-1}$, (ii) short exposure; laser frequency $16\,011\text{ cm}^{-1}$, (iii) long exposure; laser frequency $16\,005\text{ cm}^{-1}$

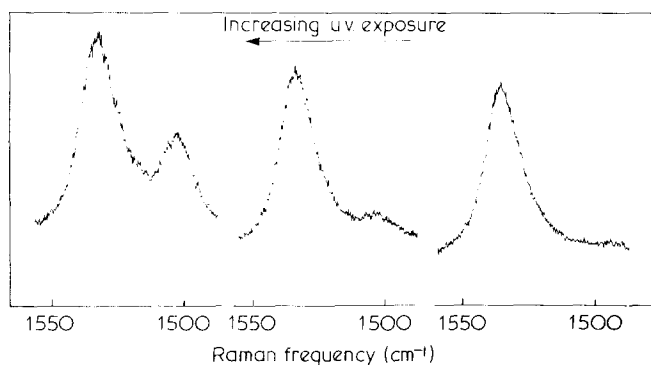


Figure 5 Variation of C=C stretching vibration in resonant Raman spectra of u.v. irradiated BCl crystals with time of u.v. exposure

Similar conclusions are derived from the Raman spectra. Resonant scattering occurs because of the proximity of the frequencies of the laser radiation and the excited π electron state of the polymer backbone. This simplifies the spectrum since only the backbone vibrations are enhanced by the process, thus the C=C and C≡C stretching vibrations are the principal features of the spectrum²¹. Figure 4 shows that for BCl after a short period of u.v. irradiation, the C≡C and C=C vibrations have single peaks, insensitive to laser frequency. This agrees with the appearance of a single bond π absorption, characteristic of a single polymeric species. It can be seen, however, that long exposure to u.v. irradiation gives rise to additional features in the spectrum paralleling the appearance of an additional band in the optical spectrum. Figure 5 shows more clearly the growth of the additional lines for the C=C stretching vibration for BCl, with increasing u.v. exposure and therefore polymer content. We obtain similar results for other monomers of the series, for example the bis(laurate ester) (BL), shown in Figure 6. Shown here also is the spectrum of the polymer residue. The prominent band for the residue is similar but not identical with the lower frequency band of the non-extracted material which appears after prolonged u.v. irradiation of the monomer. Extracted BCl residues have similar Raman spectra (Figure 7), and the use of different laser frequencies shows that the low frequency peak has a marked resonance in the vicinity of the absorption edge of the extract. These features can be interpreted as follows. On extraction, the polymer relaxes, its absorption energy is red shifted, and a new set of Raman frequencies resonating at the new absorption energy are observed. However, some polymer still retains the conformation it had in the monomer matrix. At low conversion

the polymer is in equilibrium with the host lattice but it begins to segregate from the matrix as conversion increases. The segregated polymer is not fully relaxed since neither the optical nor Raman spectra of the segregated species are the same as those of polymer extract. More detailed Raman spectra studies are in progress and a fuller report will be published elsewhere.

The changes in the optical and Raman spectra are compatible with the colour changes observed during polymerization. The parallel with 2,4-hexadiyne-1,6-diol is clear where initially-formed polymer anneals, segregates from the matrix and destroys product crystallinity^{17,18}. However, for the esters, the packing of the side groups will prevent a full relaxation of the polymer and it is necessary for the side groups to be disordered for relaxation to be possible. The extraction process, using a relatively weak solvent such as acetone, clearly cannot disorder the side groups in crystalline aggregates of polymer and hence the extract retains a component similar in form to the polymer in the monomer matrix.

Possible monomer structures

X-ray structural analysis has not been attempted so far because of the generally microcrystalline nature of the samples. This is a common problem with organic materials containing long-chain paraffinic groups. However, some possible structures can be deduced from a study of molecular models. Since monomer conformation has been shown to

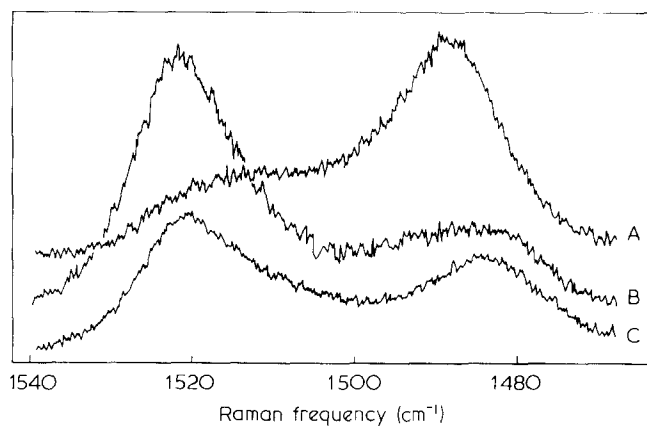


Figure 6 Resonant Raman spectra of BL. (i) insoluble polymer residue (ii) irradiated crystals; short exposure (iii) u.v. irradiated crystals; long exposure

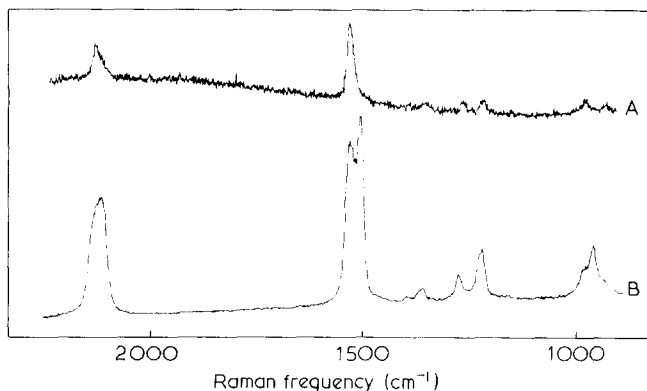


Figure 7 Resonant Raman spectra of insoluble, extracted BCl polymer residue (i) laser frequency $19\,433\text{ cm}^{-1}$, (ii) laser frequency $16\,001\text{ cm}^{-1}$

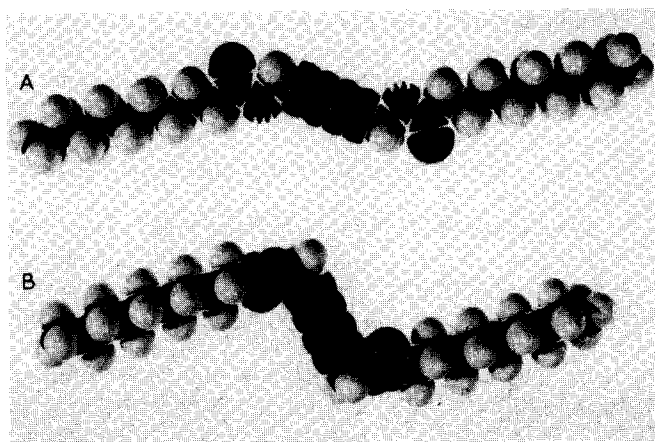


Figure 8 Molecular model possibilities for BCI (i) inactive form (ii) active form

be important, we have considered the two possible forms for the BCI monomer shown in Figure 8. Conformation A, the more linear representation, has no steric hindrance but such model monomer molecules pack with considerable free volume and the diacetylene units are poorly placed for polymerization, in terms of the criteria indicated in Figure 1. The second structure, B, is formed by rotation of the side group about the $\text{CH}_2\text{-O}$ bond linkage. This results in some bond strain about this linkage, but the crystal packing of the paraffinic chains is better and the diacetylene units are well placed in terms of the criteria of Figure 1, so that the solid state reactivity will be much higher. We postulate therefore that for the bis-caproate (BCO) and bis-caprylate (BCY) esters the monomer crystals consist of molecules with the less reactive conformation, i.e. structure A, but for BCI and higher members of the series, the reactive conformation, i.e. structure B, is adopted. The gradually decreasing reactivity with increasing length of side chain can then be ascribed to the greater resistance that the interaction of the side chains present to the molecular reorganization necessary for solid-state polymerization. Work is continuing to obtain samples suitable for X-ray structural studies in order to provide a critical test of this hypothesis.

It is clear that conformations in which the side group chains become disordered will be much less reactive because of the larger intermolecular distances that must arise from this. Free rotation or kink formation in the solid state as observed in pure paraffins¹¹ is unlikely in this case because of the bulk of the central diacetylene unit and the low melting points of the monomers. Marked changes in optical and Raman spectra occur for the salts of asymmetric monomers with the carboxylic acid moiety at the end of the molecule, which have sufficiently high melting points for the side groups to disorder in the solid state^{22,23}. It is apparent from the results for polymer extracts that some such disordering of the side groups is necessary to obtain a fully relaxed chain in the esters.

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