lecular weight fraction, the proportion of the slower modes does not decrease, but their identity becomes blurred into a very broad peak(s) at the slow end of the delay time spectrum, and this is more accentuated as the concentration is raised. This is in part due to the effects of polydispersity and also coupling of modes in the heavily entangled system.

These findings support the results obtained on semidilute solutions of polystyrene in ethyl acetate and also cyclohexane. Taken together the results establish a complex solution structure, at least in poorer solvents. The ongoing work is directed toward further elucidation of the character of the slower modes.

It is known that at high polymer concentrations (and in polymer melts) the photon correlation spectrum becomes K independent and may be interpreted as a wide distribution of internal modes.[31] Our interpretation of the middle and slow modes is that they represent cooperative internal relaxation modes of many entangled chains. At high segment concentrations, the internal modes have become slower than the collective diffusion motions of the network[32] and will eventually dominate the spectrum. A comprehensive theory for the relative amplitudes and relaxation times in concentrated solutions is not available, however.

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Thermotropic Liquid Crystalline Main-Chain Polyesters Containing Cyclooctyl Units. 4. Influence of the Methylene Spacer Length on the Nature of the Mesophase

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ABSTRACT: A series of polymers based on the novel mesogenic unit *cis*-1,5-cyclooctanediyl bis(*p*-hydroxybenzoate) have been synthesized with spacer units varying from 3 to 10 methylene units. Only smectic phases could be detected when 3, 4, and 10 methylene units were incorporated and this changed to nematic phases only when the space lengths were 5–9 units. The smectic phase could be changed to a chiral nematic one when an optically active molecule (+)-3-methyladipic acid was incorporated in the chain. An odd–even effect in the melting and clearing temperatures was detected as the spacer length changed, with higher values being obtained when there was an even number of methylene units in the spacer. Supercooling effects could also be observed.

Introduction

Rigid polymers which show a high degree of molecular order either in solution (lyotropic) or in the melt (thermotropic) are characterized by their unique optical properties analogous to low molecular weight liquid crystals.[1,2] Fibers spun from orientated liquid crystalline (LC) states are claimed to have superior mechanical strength[3] because of the orientation of the molecules and so this characteristic property can be very attractive in such systems. As a consequence, the relationships between the structure and the properties of liquid crystalline polymers have been extensively studied, and progress in this area has recently been reviewed.[4]

Main-chain liquid crystalline polymers usually consist of aromatic units which act as the rigid component, the mesogen, and the thermal transition temperatures of these

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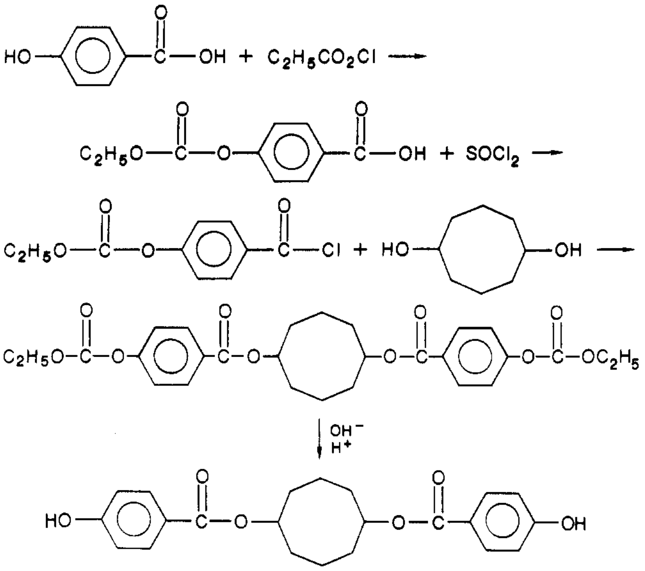
polymers can be reduced by incorporating flexible spacers as predicted by de Gennes.[5] The variety of aromatic units which act as suitable mesogens is rather limited and the behavior of the polymer very often depends upon the properties of the linking group.[4]

We have already reported briefly on the use of cyclooctyl moieties as part of the mesogenic group,[6] and the dual role of the eight-membered ring as both a rigid unit and a flexible spacer has also been discussed.[7] Here, we shall report in greater detail on the effect of flexible spacers on this new series of liquid crystalline polyesters.

Experimental Section

The novel monomer *cis*-1,5-cyclooctanediyl bis(p-hydroxybenzoate) (COHB) was synthesized according to the following scheme.



Monomer Synthesis. *p*-[(Ethoxycarbonyl)oxy]benzoic Acid (I). Ethyl chloroformate (50 cm^3) was added to a chilled (0 °C) solution of *p*-hydroxybenzoic acid (60 g, 0.434 mol) and sodium hydroxide (38 g, 0.955 mol) in 900 cm^3 of water. The reaction mixture was then acidified with 2 M HCl and the precipitate was filtered, washed with excess water, and recrystallized from a water/acetone mixture: yield 90%; mp 158 °C.

***p*-[(Ethoxycarbonyl)oxy]benzoyl Chloride (II).** Compound I (20 g, 0.095 mol) was refluxed with thionyl chloride (15 g, 0.126 mol) and two drops of dimethylformamide. The excess thionyl chloride was distilled off, and the crude product was recrystallized from hexane: yield 80%.

***cis*-1,5-Cyclooctanediyl Bis[*p*-[(ethoxycarbonyl)oxy]benzoate] (III).** *cis*-1,5-Cyclooctanediol (ALDRICH) (6.3 g, 0.028 mol) was added to a solution of compound II (2.0 g, 0.014 mol) in 20 cm^3 of 1,2-dichloroethane. The mixture was refluxed overnight under a nitrogen atmosphere, then extracted into toluene, and dried with anhydrous $MgSO_4$. The solvent was distilled off and the product was recrystallized in ethanol: yield 70%; mp 90 °C; ^{1}H NMR ($CDCl_3$ and TMS) 1.50 (t, CH_3), 1.95 (m, cyclic CH_2), 4.25 (q, CH_2), 5.10 (s, CH), 7.05, 7.85 (d, Ar) ppm.

***cis*-1,5-Cyclooctanediyl Bis(*p*-hydroxybenzoate) (IV).** Compound III (6.0 g, 0.011 mol) was dissolved in 20 cm^3 of ethanol and treated with 12 cm^3 of 2 M NaOH solution on a steam bath for 30 min. The excess ethanol was evaporated, and the residue was adjusted to pH 7 with 10% acetic acid, filtered, dried, and recrystallized from a water/ethanol (1:1) mixture: yield 46%; mp 197 °C; ^{1}H NMR (acetone-*d* and TMS) 1.90 (m, cyclic CH_2), 5.10 (s, CH_2), 6.75, 7.75 (d, Ar) ppm.

Polymer Synthesis. Monomer IV was reacted with stoichiometric amounts of the appropriate diacid chloride in tetrachloroethane. The mixture was stirred at room temperature under a nitrogen atmosphere for 24 h and then poured into 200 cm^3 of methanol. The precipitated polymer was washed with methanol and digested in 20% Na_2CO_3 solution for 4 h, filtered, washed with dilute HCl and then water, and finally dried under vacuum at 60 °C. The polymers were characterized by conventional methods.

Table I
Characteristic Phase Temperatures for the COHB Series of Polymers

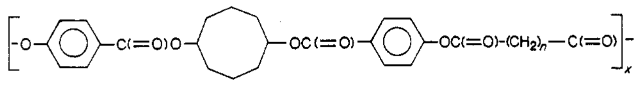
methylene units	yield, wt %	$[\eta]^a$	T_g, K	T_m, K	T_i, K^b	T_i, K^c	ΔT
3	89	0.135		335	366	357	29
4	92	0.100	342	393	417	388	24
5	95	0.130	310	352	358	350	8
6	86	0.130	304	366	389	365	23
7	94	0.190	309	349	375	370	26
8	90	0.105		338	348	333	10
9	87	0.175	300	341	355	352	14
10	96	0.500	301	367	396	378	7

[a] Intrinsic viscosity in chloroform at 298 K, units in dL/g. [b] Heating. [c] Cooling.

Other Techniques. Mesophases were identified by using a Reichert Thermovar polarizing microscope fitted with a hot stage (magnification 100×). Thermal analyses were recorded by using a Perkin-Elmer DSC-2 differential scanning calorimeter at a heating and cooling rate of 20 K/min. Indium standards were used for temperature calibration. Viscosity measurements were performed in chloroform solution at 25 °C by using a Cannon-Ubbelhode viscometer.

Results and Discussion

The polymers are identified by the code letters COHB-*n*, where *n* is the number of methylene units in the aliphatic acid. The general structure of these polymers is



Polymerization conditions and the properties of the polymers under investigation are summarized in Table I. The polymer products were obtained in good yield and were characterized by values of intrinsic viscosity in the range $[\eta] = 0.1–0.5$; however, the precise values of the molecular weight were not measured.

Optical studies showed that both nematic and smectic mesophases were exhibited. Identification of these was made predominantly by optical observation of the textures developed which were then compared with known systems.

Smectic Polymers. Three polymers were obtained which exhibited only smectic phases when there were 3, 4, and 10 methylene units in the spacer.

In a previous report[6] on polymer COHB-4 two, smectic phases were identified from the presence of the batonnet (smectic A) and the mosaic (smectic B) textures, and so the transition sequence of polymer COHB-4 is

$$\mathrm{k} \xrightarrow{393\ \mathrm{K}} \mathrm{S_B} \xrightarrow{405\ \mathrm{K}} \mathrm{S_A} \xrightarrow{417\ \mathrm{K}} \mathrm{i}$$

where k represents the crystalline state and i the isotropic state.

Similar mesophases were also observed in polymer COHB-10 except that the transition temperatures are in a slightly lower temperature region. Microscopic observation showed a batonnet and mosaic texture at 380 K, suggesting the existence of both smectic A and smectic B phases, and the mesomorphic order of polymer COHB-10 is believed to change with temperature in the sequence

$$\mathrm{g} \xrightarrow{300\ \mathrm{K}} \mathrm{k} \xrightarrow{367\ \mathrm{K}} \mathrm{S_B} \xrightarrow{381\mathrm{K}} \mathrm{S_A} \xrightarrow{396\ \mathrm{K}} \mathrm{i}$$

where g represents the glassy state. The corresponding differential scanning calorimetry (DSC) thermograms for COHB-10 are shown in Figure 1, with T_g at 300 K and two peaks at 396 K and 381 K. Melting was best observed microscopically at 367 K.

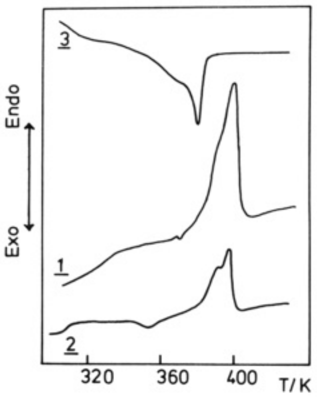


Figure 1. DSC thermograms for sample COHB-10: curve 1 first heating; curve 2 second heating; curve 3 cooling.

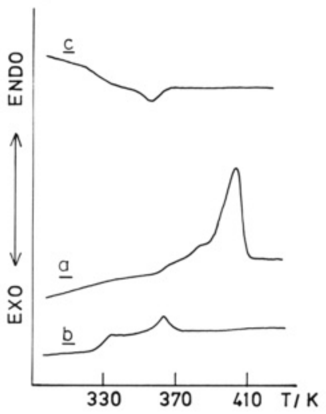


Figure 2. DSC thermogram of polymer COHB-3: (a) first heating scan; (b) second heating scan; (c) first cooling scan.

Table II
Calorimetric Data for the COHB Polymers

methylene units	T_i, K	ΔH_i, kJ/mol	ΔS_i, kJ/mol
3	366	1.80	1.18
4	417	11.57	6.64
5	358	1.24	0.84
6	389	4.17	2.57
7	375	2.65	1.71
8	348	2.44	1.67
9	355	2.92	1.97
10	396	9.45	5.71

Apart from the distinguishable optical textures observed, the existence of highly ordered smectic phases was further supported by the very high values for the changes in enthalpy (ΔH_i) and entropy (ΔS_i) at the transition temperature for polymers COHB-4 and COHB-10. These are obtained by measuring the heat capacity change, assuming that the mesomorphic to isotropic transition (T_i) is an equilibrium state, and are listed in Table II.

The DSC thermograms of polymer COHB-3 are shown in Figure 2. A large endothermic transition between 360 and 415 K with a maximum at 406 K was detected in the first heating scan (curve a). In the second heating scan (curve b), the highest peak dropped about 40 K to 366 K. It was because of this enormous change that the heating scan was repeated for a further three times, but no sign of subsequent alteration in the thermogram was seen. A glass transition was not detected and T_m was finally assigned at 335 K after repeated scanning.

When polymer COHB-3 was cooled from its isotropic state to 363 K and annealed at this temperature for 24 h, a focal–conic texture was developed from the homeotropic phase. This unique change can only be a result of the formation of a smectic A phase. Unlike polymers COHB-4 and COHB-10, the mosaic texture which characterizes the smectic B phase was not observed. The sample was reheated and again cooled from the isotropic state to 358 K where it was maintained at this temperature for 2 h, during which time a blurred schlieren (sandlike) texture, resembling the smectic C phase found in low molecular weight liquid crystals, was seen to develop.[8] Further evidence to support our speculation of a smectic C phase was the change of birefringence colors from a pale-grey yellow to a rust-blue on cooling.[8] Hence, the mesomorphic changes characteristic of polymer COHB-3 are

$$\mathrm{k} \xrightarrow{335\ \mathrm{K}} \mathrm{S_C} \xrightarrow{358\ \mathrm{K}} \mathrm{S_A} \xrightarrow{366\ \mathrm{K}} \mathrm{i}$$

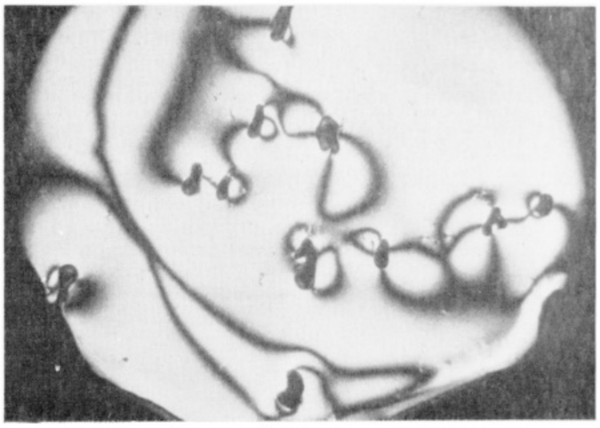


Figure 3. Microphotograph of polymer COHB-5 taken at 353 K, showing the schlieren texture of a nematic phase.

Chiral Nematic Polymer. There was no evidence of a nematic phase in any of these polymers with $n = 3$, 4, and 10, but this can be changed by small structural alterations.

Asrar et al.[9] have demonstrated that a smectic phase can be destabilized by disrupting the regularity along the backbone chain; thus a cholesteric phase was observed when the linear spacer was diluted with (+)-3-methyladipic acid (MAA). Meurisse et al.[10] also found that using branched flexible spacers had the effect of broadening the molecules and increasing the separation of the long axes of the neighboring molecules. In order to examine this effect, polymer COHB–MMA was prepared, which had the same number of atoms between the mesogenic groups as polymer COHB-4 but differed in that MAA is methyl substituted and optically active. Thermal analysis revealed that polymer COHB–MAA had a glass transition at 327 K and a clearing transition at 388 K. As anticipated there was a pronounced decrease in the temperatures of the transitions, but there was also a change in mesophase and a chiral nematic phase could be identified optically in polymer COHB–MMA in contrast to the smectic A and B phases exhibited by polymer COHB-4.

Nematic Polymers. The other polymers in this series with $n = 5$–9 all show nematic mesophases. Figure 3 illustrates a schlieren texture of polymer COHB-5 when cooled from the isotropic melt to 353 K. This texture, observed between crossed polarizers, displayed dark brushes which have irregular curved shapes. At some points, two dark brushes meet, and at others, clusters of four brushes meet. From the observation of points at which only two dark brushes meet, the mesophases can be identified unambiguously as a nematic phase.[8] The nematic mesophase differs from smectic mesophases in that it only has orientational order rather than orientational and positional order; hence, they are more sensitive to

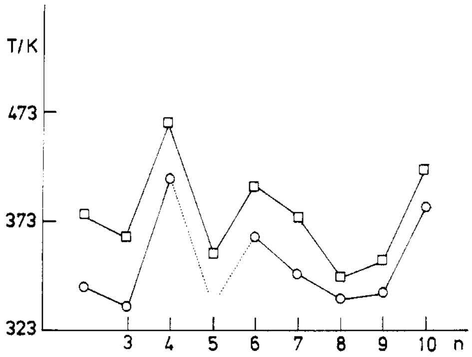


Figure 4. Plot of melting temperatures (○) and clearing temperatures (□) against spacer length.

shearing and other external stimuli. For example, immediately after the melting of polymer COHB-7, a large number of threads were observed when the sample was viewed microscopically, which gradually disappeared when the temperature was near the isotropic transition, and a gentle shear produced a homogeneous greenish blue color across a large area.

Odd–Even Effect. The effect of increasing the length of the flexible spacer units on the properties of main-chain LC polymers has been well documented for other polymers.[11-15] Essentially three effects can be observed: (1) reduction of the transition temperatures (both melting and clearing) with increased spacer length; (2) an odd–even relationship for the transition temperatures, in which polymers with an even number of atoms in the spacer generally have higher transition temperatures than those in the same series with an odd number of atoms; and (3) in some cases, a smectic mesophase is formed by polymers containing very long spacers.

In this series of polymers both the melting points and the clearing points measured by DSC are gradually decreased in a zigzag manner as n is increased to 7 or 8 but they then appear to increase beyond that value. These effects are illustrated in Figure 4. As commonly observed, the polymers with an even number n of methylene units show higher melting points than those with an odd number n.

The minimum at $n = 8$ is intriguing, and a similar phenomenon was also observed by Ober et al.,[16] who suspected that it was due to the formation of a smectic phase, but such a phase could not be observed by them using other characterization methods. For polymer COHB-8, only a threaded nematic texture was observed and there was no sign of any smectic phases like those found in polymers COHB-3, -4, and -10. The absence of an ordered smectic phase was also reflected by the low enthalpy and entropy changes at the clearing temperature. More recently, Braun and Schulke prepared a series of polymers which are structurally similar to our series except that the cyclooctyl unit is replaced by a cyclohexyl unit and the nature of the mesophase was not disclosed, but a consistent odd–even effect from $n = 4$ to $n = 8$ was reported.[13]

Literature values are now available for the clearing enthalpy (ΔH_i) of several hundred nematic compounds.[17] These values fall in the region of 0.08–9.6 kJ/mol, with a typical value of slightly less than 2.1 kJ/mol. Despite the relatively lower value for polymer COHB-5, the average value of ΔH_i for the nematic polymers is 3.05 kJ/mol which is 23% higher than that of the typical low molecular weight liquid crystals. Entropies for the nematic polymers also show a similar trend. This observation suggests that the order present in the polymeric mesophase is higher than that found in low molecular weight liquid crystals.

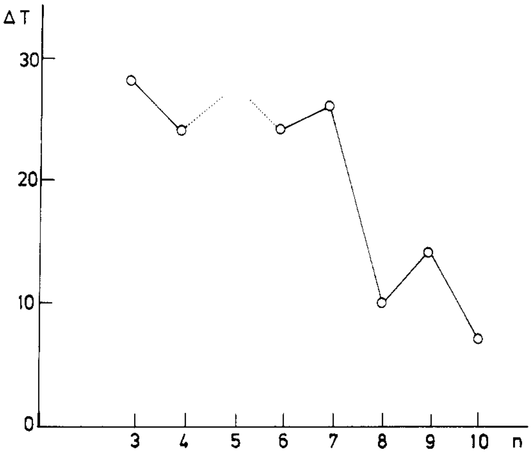


Figure 5. Plot of mesophase interval ($\Delta T = T_i - T_m$) against spacer length.

The abrupt change of mesophase from $n = 4$ (smectic) to $n = 5$ (nematic) is difficult to understand. A possible explanation may be that there are reduced degrees of freedom of configuration resulting from the shorter spacer length and the probability of one mesogenic core imposing a dipole–dipole interaction on another in the immediate vicinity is greatly increased. As a consequence, the rigid units are able to pack more easily into layers. In the case of polymer COHB-10, formation of the smectic mesophase may be attributed to folding of the longer methylene chain which encourages a greater degree of ordering in the system.

The enthalpic change (ΔH_i) for polymer COHB-3 is a mere 1.80 kJ/mol, which is very much smaller when compared with the other smectic polymers. Apart from the odd–even effect, which should be taken into account, the main cause is that the enthalpy associated with the transition from the smectic C phase to smectic A phase is very small and sometimes almost undetectable by DSC.[8]

The mesophase intervals of COHB polymers are illustrated in Figure 5 where the parameter, ΔT, is defined as the difference between the clearing (T_i) and melting (T_m) temperatures. As shown in Figure 5, ΔT oscillates in an odd–even fashion. The temperature range over which the mesophase existed was consistently broader for the polymers with an odd n value as compared with those with an even n value. A similar phenomenon was also observed by Ober et al.,[16] and these authors attributed this to the variation in the length of the spacer groups having a greater effect in decreasing T_m and T_i, particularly among the polymers with an odd number of polymethylene units. Their argument was based on the higher enthalpic and entropic values observed for the odd-number series, despite the fact that both the clearing and the melting transition of the even numbers are higher than those of the odd numbers. The thermodynamic parameters reported are generally in agreement with those for our COHB series in that ΔH_i and ΔS_i for the even-numbered spacers are higher than those for the odd-numbered polymers.[11,18]

Most of the published reviews indicate that a supercooling effect in liquid crystalline polymers is generally detected in the mesophase to crystal transition. This is assisted by the highly viscous nature of these polymeric liquid crystals, and there is now more evidence to suggest that this effect can also happen on moving from the isotropic to mesomorphic state.[13,19] A consistent decrease in the supercooling effect when the spacer length increases has been observed here (see Figure 6) also; this effect is more prominent for the even-numbered members of the series. One of the remarkable features of LC polymers is

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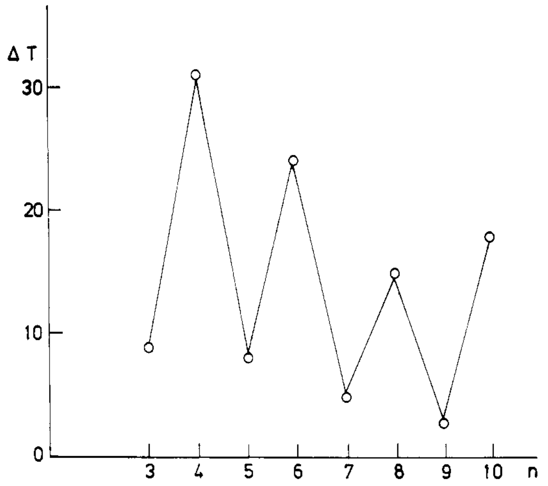

Figure 6. Plot of supercooling effect ($\Delta T = T_i - T_l$) against spacer length.

that the mesomorphic order can be locked into the glassy state by quenching rapidly from the isotropic phase. Such pretransitional order induced by this mechanical shock might be one of the contributing factors to this unusual effect on making the isotropic to the mesomorphic transition.

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Registry No. I, 15552-32-6; II, 57045-26-8; III, 106610-62-2; (IV)(ClCO(CH$_2$)$_3$COCl) (copolymer), 115339-58-7; (IV)(ClCO(CH$_2$)$_3$COCl) (SRU), 115339-51-0; (IV)(ClCO(CH$_2$)$_4$COCl) (copolymer), 106608-01-9; (IV)(ClCO(CH$_2$)$_4$COCl) (SRU), 106707-10-2; (IV)(ClCO(CH$_2$)$_5$COCl) (copolymer), 115339-59-8; (IV)(ClCO(CH$_2$)$_5$COCl) (SRU), 115339-52-1; (IV)(ClCO(CH$_2$)$_6$COCl) (copolymer), 115339-60-1; (IV)(ClCO(CH$_2$)$_6$COCl) (SRU), 115339-53-2; (IV)(ClCO(CH$_2$)$_7$COCl) (copolymer), 115339-61-2; (IV)(ClCO(CH$_2$)$_7$COCl) (SRU), 115339-54-3; (IV)(ClCO(CH$_2$)$_8$COCl) (copolymer), 115339-62-3; (IV)(ClCO(CH$_2$)$_8$COCl) (SRU), 115339-55-4; (IV)(ClCO(CH$_2$)$_9$COCl) (copolymer), 115339-63-4; (IV)(ClCO(CH$_2$)$_9$COCl) (SRU), 115339-56-5; (IV)(ClCO(CH$_2$)$_{10}$COCl) (copolymer), 115339-64-5; (IV)(ClCO(CH$_2$)$_{10}$COCl) (SRU), 115339-57-6; (COHB)(MAA) (copolymer), 115339-65-6; ethyl chloroformate, 541-41-3; *p*-hydroxybenzoic acid, 99-96-7; *cis*-1,5-cyclooctanediol, 23418-82-8.

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A New Theory of Entanglements and Dynamics in Dense Polymer Systems

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ABSTRACT: The entanglement concept, which is central to the reptation theory, has been reformulated. The phenomenological parameter, N_e, introduced by de Gennes and Doi and Edwards, has been replaced by a new parameter, $\tilde{N}$, called the coordination number, which can be computed from the conformational statistics of many chains, in a melt or concentrated solution. It is argued that, with the appropriate choice of $\tilde{N}$, one can relate this quantity to the mean entanglement spacing according to a simple relation. $\tilde{N}$, which is a preaveraged topological parameter, also provides a criterion for the presence of entanglements and describes the degree of entanglement in terms of the chain parameters and polymer density. The mean entanglement spacing is shown to depend on the degree of polymerization in the region of the transition. The transition from entangled to unentangled behavior, which is geometrical in origin, follows from this theory as do several well-established scaling laws for melts and concentrated solutions. A generalized Rouse model (GRM), modified to incorporate entanglement effects, has been used with this theory to describe polymer dynamics in entangled and unentangled melts. The reptation theory results are recovered in the asymptotic long-chain limit.

1. Introduction

Recently, the mechanical and transport properties of polymer melts and concentrated solutions have been of considerable experimental and theoretical interest.[1] Despite the chemical and structural diversity of linear polymeric systems, most exhibit universal behavior in their rheological properties that is depicted in Figure 1. For low molecular weight melts, the zero shear viscosity, η_0, is proportional to the degree of polymerization, N, whereas for high molecular weights, the zero shear viscosity scales as some higher power of N, typically $N^{3.4}$. The transition occurs at a degree of polymerization, N_c, which varies from one polymer to the next. It is now well-known that this change in the scaling law can be attributed to the formation of entanglements amongst chains in the high molecular weight regime.

Most theories, for the dynamics in these systems, are of the mean field type in that they focus on the motion

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