the gel network, and (c) sterically imposed incompleteness of the curing reactions so that either unreacted epoxy or unreacted amine groups are trapped in the cured epoxy network.

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Registry No. DGEBA (homopolymer), 25085-99-8; DDH, 13093-04-4; METAMIN, 42585-33-1; PYRODDH, 87655-74-1; TEMPENE, 2564-83-2.

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NMR Study of Nematic Order of Semiflexible Thermotropic Polymers

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ABSTRACT: Chain conformations and orientational order parameters in the nematic state of the deuterium-labeled thermotropic polyester $(C_{10}D_{20}OC_6H_4COOC_6H_4OC_{10}D_{20}OC_6H_4OOCC_6H_4O)_x$ are determined by deuterium (D) NMR and H NMR methods. The D NMR spectra show one quadrupole splitting in the nematic state, indicating that only a specific set of chain conformations are admitted for $C_{10}D_{20}$ spacer groups. They are found to comprise those conformers that place every second bond starting from the OCD_2 attached to the rigid (phenylene) unit almost exclusively in the trans state. From the magnitudes of quadrupole splittings, the orientational order parameters of chain segments, the alignment axis of which virtually coincides with the axis of rigid (phenylene) units for these conformers, are found to fall around 0.8 and extrapolate to ca. 0.75 at the nematic–isotropic transition. Separate determination of orientational order parameters of the rigid aromatic units from H NMR dipolar splittings yields the order parameters in excellent agreement with those derived from D NMR results, and thus validates our interpretation of D NMR spectra in terms of the specific conformational order. The conformational order thus elucidated by NMR study therefore supports the previous conclusion of Yoon and Bruckner, who proposed that the poly(methylene) spacers assume highly extended configurations in the nematic state upon considering the enthalpies and the entropies of isotropic–nematic transitions of thermotropic polymers comprising rigid groups connected by poly(methylenes).

Introduction

The molecular order in the liquid crystalline state of polymers has been the subject of a considerable number of publications in recent years.[1-7] For polymer liquid crystals the specific questions are concerned not only with the orientational order parameter, which is well studied for monomer liquid crystals, but more importantly with the ordering, or selection, of chain conformations for the flexible sequences in the liquid crystalline state.[20]

A number of experimental results point to rather high degree of conformational and orientational order in polymeric nematogens, compared to those of their monomeric counterparts. For example, polymeric nematogens comprising poly(methylene) spacers exhibit much larger enthalpy and entropy changes at isotropic–nematic transitions as well as greater oscillations in clearing temperatures with the even–odd alternation of the number of methylene units of the spacers.[4,8,9] In a recent paper[1] (which will be designated as I hereafter) Yoon and Bruckner, upon comparing the isotropic–nematic transition characteristics with the distribution of chain sequence extension, concluded that the stability of the nematic state and the concomitant

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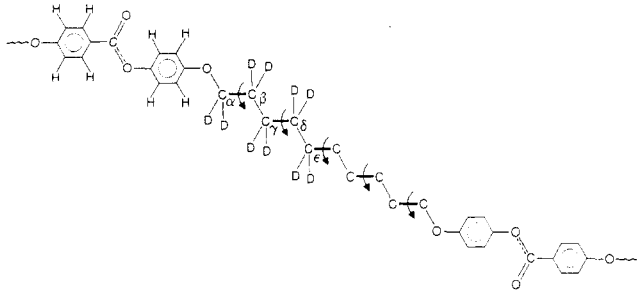

Figure 1. Schematic diagram of the labeled chain sequence and conformations in the nematic state. The bold lines with arrows denote the bonds around which the trans, gauche$^+$, and gauche$^-$ states are allowed in proportion to their statistical weights. All the other bonds between the rigid (phenyl benzoate) groups are in the trans conformation.

conformational ordering is determined primarily by the relative population (i.e., configurational partition function) of highly extended conformers, which are favored for packing purposes. Moreover, for the polymers comprising linear rigid groups and even-numbered poly(methylenes) connected through ether linkages, the experimental results of enthalpy and entropy changes were consistent with the idea that only a set of highly extended conformers are selected in the nematic state. These conformers are found to place every second bond starting from the OCH_2 attached to the rigid (phenylene) unit in the trans state, while the intervening bonds are allowed to assume trans, gauche$^+$, and gauche$^-$ states according to the corresponding statistical weights: they are illustrated schematically in Figure 1.

The conformational order thus proposed is based on macroscopic thermodynamic properties. A spectroscopic investigation that can provide the information on a molecular level is hence called for in order to verify such a conformational order. In this paper we apply the deuterium (D) NMR method to investigate primarily the conformations of the labeled thermotropic polyester $(C_{10}D_{20}OC_6H_4COOC_6H_4OC_{10}D_{20}OC_6H_4OOCC_6H_4O)_x$ in the nematic state. The general pattern, or profile, of the D NMR quadrupole splitting of this polymer is related to the nematic conformations of $C_{10}D_{20}$ groups. Once the conformations are determined, the absolute magnitudes of quadrupole splittings then lead to the assignment of orientational order parameters (see below). Moreover, independent measurements of order parameters from H NMR dipolar splittings of this labeled polymer provide the means of validating the interpretation of D NMR spectra.

Measurements of orientational order parameters in the nematic state of thermotropic polymers were carried out previously with H NMR,[3] diamagnetic anisotropy,[2,4] ESR,[5] and IR dichroism[6] methods. The study of conformational order of polymeric nematogens using D NMR in combination with H NMR has recently been reported by Samulski et al.[7] Although the prevalence of certain configurations is indicated by these authors, the specific nature of the conformational order was not ascertained definitely.

Determination of Conformational and Orientational Order by D NMR and H NMR

In the nematic state aligned under the applied magnetic field, the D NMR spectra of deuterium-labeled polymers reflect the incomplete orientational averaging of the interaction of the quadrupole moment of the deuteron with the local electric field gradient tensor. Since the electric field gradient tensor of the C–D bond is nearly uniaxially symmetric with its principal axis along the C–D bond, the quadrupole splitting for a given C–D bond in uniaxially

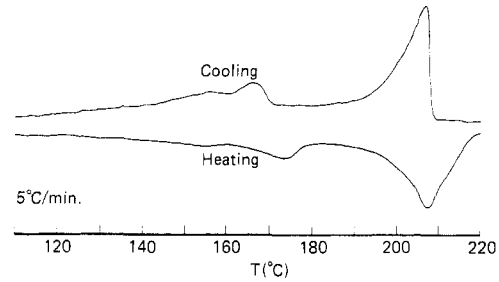

Figure 2. DSC traces of the labeled polymer during heating and cooling at 5 °C min^{-1}. The peak around 210 °C is from the isotropic–nematic transition and the one around 170 °C is due to the nematic–crystalline transition.

symmetric systems can be expressed in the fast-motion limit by[7,10]

$$\Delta\nu_i = \frac{3}{2}\left(\frac{e^2qQ}{h}\right)s\left\langle\frac{3\cos^2\phi - 1}{2}\right\rangle \qquad (1)$$

where e^2qQ/h (=174 kHz[11]) is the quadrupolar coupling constant, s denotes the (orientational) order parameter of chain segments with respect to the director of the nematic domain, ϕ represents the angle between the C–D bond and the alignment axis of chain segments, and the brackets denote the averaging over all the allowed conformations.

For the $C_{10}D_{20}$ group of interest here, there are five distinguishable CD_2 units, labeled α, β, γ, δ, and ϵ in Figure 1. The relative positions of these five quadrupolar splittings therefore reflect the nematic chain conformations. Once the relative positions, or profiles, of D NMR spectra are matched by a suitable set of conformations, the absolute magnitudes of quadrupole splittings then lead to the assignment of order parameters according to eq 1.

The H NMR spectra from the deuterium-labeled chain segments of Figure 1 are dominated by the dipolar interactions between the two vicinal protons of the phenylene group. If the major alignment axis of chain segments coincides with the phenylene–O bond (see below), the magnitude of this dipolar splitting can then be approximated in the fast-motion limit of uniaxially symmetric systems by[12]

$$2\delta_\nu = \frac{3}{2\pi}\frac{\gamma^2h}{r_{H\text{-}H}^3}s \qquad (2)$$

where γ is the gyromagnetic ratio of the proton, h is the Plank constant, and $r_{H\text{-}H}$ denotes the distance between two vicinal protons of the phenylene group. Taking $r_{H\text{-}H}$ to be 2.45 Å leads to a value of 24.5 kHz for the case of perfect alignment. The H NMR method thus provides an independent means of determining the order parameter. Comparison of the order parameters from D NMR and H NMR results, respectively, can therefore be used to confirm the deduction of conformational order from the D NMR spectra.

Experimental Procedure

Sample Preparation. The polymer was prepared by the interfacial polyesterification of 4,4-bis(chloroformyl)-1,10-diphenoxydecane-d_{20} and 4,4-dihydroxy-1,10-diphenoxydecane-d_{20} as described in detail previously.[8] Rough fractionation was then carried out by first removing the high molecular weight fraction that is insoluble in m-cresol upon heating to ca. 100 °C by centrifugation. The soluble fraction was then precipitated with glacial acetic acid at room temperature and then washed thoroughly with chloroform. This fractionation resulted in a sharper isotropic–nematic transition peak around 210 °C in DSC measurements (see Figure 2), so that the overlap with the crystallization peak around 170 °C was reduced substantially.

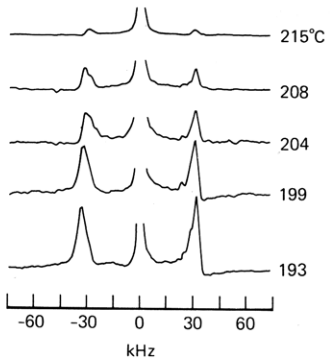

Figure 3. Traces of D NMR spectra of the labeled polymer (shown in Figure 1) at various temperatures of the nematic region reached by heating the sample through the crystalline–nematic transition.

NMR Measurements. NMR spectra were obtained with a Bruker CXP-100 spectrometer, operated at 90 MHz (21.1 kOe) for H NMR and 14 MHz (21.4 kOe) for D NMR. Temperature control was achieved with a Bruker B-ST controller with the standard 90-MHz probe. For operation at 14 MHz a home-built probe with a 4-mm coil was constructed and the temperature was controlled with a resistively heated alumina furnace. In both cases the temperature stability was better than 1 °C.

Proton spectra were acquired with a simple $\pi/2$–FID sequence, employing quadrature phase detection. The receiver dead time was 5 μs and the digitization dwell was typically 2 μs. Signal averaging of typically 256 scans was found to give acceptable signal-to-noise ratios for the relatively small amount of sample (50 mg) used in this study. The recycle delay of 1 s was comparable to or larger than the estimated spin–lattice relaxation time over the entire temperature range of measurements (170–200 °C).

The deuterium NMR spectra were acquired with the alternating quadrupole–echo sequence, $(\pi/2)_{\pm x}$–τ–$(\pi/2)_y$–τ–echo. Such a scheme not only suppresses coherent transients due to acoustic ringing of the coil, for example, but also cancels any FID component following the second pulse which arises because the pulse lengths are not precisely $\pi/2$.[13] Data acquisition with a dwell time of 0.1–0.5 μs, depending on the temperature, was started before the echo maximum and the time-domain signal "left-shifted" prior to Fourier transformation. Quadrature detection was employed in spite of the fact that with ideal phasing the quadrature channel contributes only noise and no signal,[13] in order that the Fourier-transformed signal show both positive and negative frequency shifts. This aided in distinguishing residual coherent background from the deuterium signal. The $\pi/2$ pulse length was 4.5 μs, sufficiently short that no major correction for the finite pulse effects is required.[14] Typically 1024 scans were averaged with a recycle delay of 0.1–0.2 s. In addition, several overnight spectra were obtained in a more detailed search for weaker features.

Most spectra were taken with an echo delay time (τ) of 50 μs. This time was chosen after examining the effects of variations up to 150 μs. In the temperature range reported here there was no effect on the spectra other than an improved signal-to-noise ratio due to the decay of coherent transients (offset, of course, by the necessity of much longer acquistion times).

Results

Quadrupole Splittings of D NMR. The D NMR spectra of the labeled polymer at various temperatures of the nematic region reached by heating the sample, which was cooled previously in an aligning field of 21.4 kOe, through the crystalline–nematic transition are shown in Figure 3. The presence of central peaks, the intensity of which increases with temperature, reflects the presence of the isotropic phase coexisting with the nematic phase in our samples, most probably due to the relatively low average molecular weight and its polydispersity. It is obvious from these spectra that there exists one broad quadrupole splitting for the chains in the nematic state, and thus the

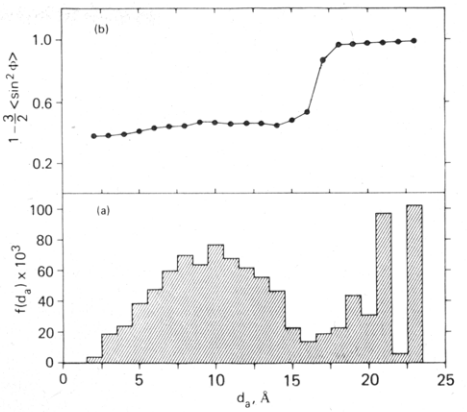

Figure 4. (a) Distribution of chain sequence extension d_a along the major extension axis. (b) Orientational correlations of two successive rigid groups with their major extension axis as a function of d_a (taken from Figure 2 of ref 1).

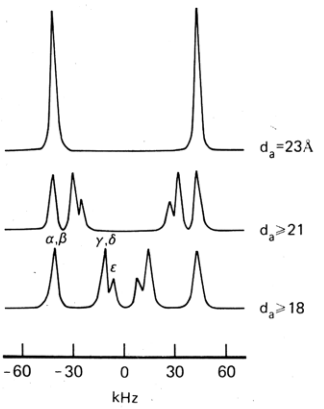

Figure 5. D NMR spectra calculated for the labeled chain segments of Figure 1 by including only those conformers whose sequence extension length d_a falls in the range indicated. The orientational order parameter is taken to be 1 in these calculations.

five CD_2 units are nearly indistinguishable in this regard. Considering the variety of conformations available to the $C_{10}D_{20}$ sequence, this result therefore indicates that the chain conformations of this ordinarily flexible group are severely restricted in the nematic state.

Following the main conclusion of I, the D NMR spectra may be analyzed by selecting the conformations on the basis of chain sequence extension. The distribution of chain sequence extension, d_a, along the major extension axis and the orientational correlations of the two rigid (phenyl benzoate) groups at the ends of a spacer with this extension axis are plotted in Figure 4 as a function of d_a, taken from Figure 2 in I; the chain sequence here refers to one rigid group and one spacer sequence. As pointed out already,[1] all the conformers with $d_a \geq 18$ Å place the two rigid groups parallel to each other; see Figure 4b. Hence, for any conformers with $d_a \geq 18$ Å the alignment axis of chain sequences will be very close to being along the rigid group, which virtually coincides with the phenylene–O axis. The quadrupole splitting for each C–D bond can therefore be calculated readily from eq 1, as long as the averaging is carried out over the conformations that fall within this interval of d_a. The D NMR spectra of the labeled polymer thus calculated taking the orientational order parameter to be 1 are shown in Figure 5. When all the conformers that place the successive rigid groups parallel to each other, i.e., those with $d_a \geq 18$ Å, are included, we predict three quadrupole splittings for the five CD_2 units as labeled in Figure 5. As we further restrict the conformers to those with longer chain sequence ex-

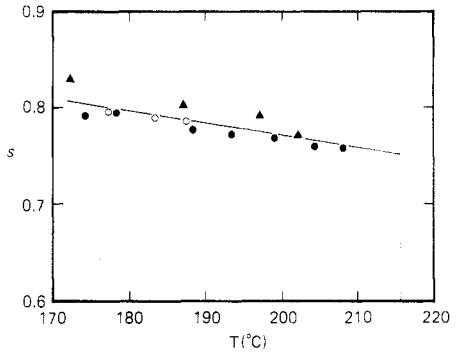

Figure 6. Orientational order parameters of the polymer in the nematic state plotted against the temperature. The filled circles represent the results determined from the D NMR quadrupole splittings in the nematic state reached by heating through the crystalline–nematic transition, and the open circles are obtained from the D NMR results for the sample cooled from the isotropic melt. The filled triangles represent the results from the H NMR dipolar splittings for the sample heated through the crystalline–nematic transition. The solid line is drawn through the experimental points to extrapolate to the nematic–isotropic transition at 215.5 °C.

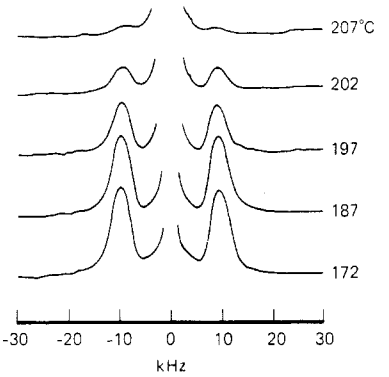

Figure 7. Traces of the H NMR spectra from the protons of the aromatic group of the labeled polymer (shown in Figure 1), obtained at the nematic temperatures indicated while heating the sample that was cooled previously in an aligning field of 21.4 kOe.

tensions, the splittings for the inner two peaks tend to increase toward the outermost one. On the other hand, the position of the outermost peak, which arises from the α and β-CD_2 groups, remains unchanged for all values of $d_a \geq 18$ Å; since the phenylene–O–CD_2–CD_2 state is always in the trans conformation,[1] this quadrupole splitting depends only on the C–C–D bond angle. Three distinct peaks always remain as this limiting sequence extension d_a increases from 18 to 21 Å.

Only when we restrict the conformers to the most extended ones with $d_a = 23$ Å (i.e., those configurations illustrated in Figure 1),[1] all the peaks merge with each othe to produce one splitting, which is consistent with the experimental profile. (For the perfectly aligned system the predicted value of this single quadrupole splitting is 84.7 kHz, taking the C–C–D angle to be 110°.) This prediction can be comprehended readily from the conformational model illustrated in Figure 1. That is, placing every second bond from the OCD_2 in the trans state puts all the C–C bonds denoted by bold lines parallel to the phenylene–O axis, regardless of the conformations assigned to the intervening bonds. Since the C–C–D bond angle is fixed, this in turn places all the C–D bond vectors tilted by the same angle from the phenylene–O axis, which is the alignment axis for these conformers, thereby producing only one quadrupole splitting for the five CD_2 groups. The comparison of the experimental spectra with the calculated ones therefore leads to the conclusion that the nematic conformations are severely restricted to the most extended ones drawn schematically in Figure 1. The profile of the experimental peaks, however, exhibits certain asymmetry with a broader shoulder in the inner frequency region. This asymmetry in the profile, which becomes more pronounced at higher temperatures, seems to indicate the presence of some less extended conformers, e.g., those with $d_a = 21$ Å. However, the fraction of these less extended conformers must be quite small, judging from the rather drastic change in the calculated spectrum upon including all the conformers with $d_a \geq 21$ Å. (The incorporation of a significant fraction of the conformers with $d_a = 21$ Å will result in the presence of well-resolved additional splittings, which are observed for the corresponding dimer as well as the polymer in the eutectic solvent.[15])

Matching the magnitude of this (nearly) single quadrupole splitting to that predicted for the extended-chain conformations with $d_a = 23$ Å then determines the orientational order parameter s according to eq 1. The order parameters obtained in this manner at different temperatures of nematic region, reached by heating the sample through the crystalline–nematic transition (filled circles) as well as cooling from the isotropic state (open circles), are plotted in Figure 6. The orientational order parameters are found to be rather high, falling around 0.8 for most temperatures, and extrapolate to ca. 0.75 at the nematic–isotropic transition.

Dipolar Splittings of H NMR. The H NMR spectra of the labeled chain sequences in the nematic state, obtained at different temperatures as the sample (cooled previously in an aligning field of 21.4 KOe) is heated through the crystalline–nematic transition, are shown in Figure 7. Again the central peaks indicate the presence of the isotropic phase that coexists with the nematic phase. The intensity of the dipolar-split peaks decreases as the temperature is increased, reflecting the decreasing fraction of the nematic portion of our sample with increasing temperature. Dipolar splittings reflect solely the orientational order of the aromatic units of the chain. They can be related to the orientational order parameters of chain segments according to eq 2, provided that the alignment axis of the chain segments coincides with the phenylene–O bond. The order parameters evaluated in this way are also plotted (filled triangles) in Figure 6 at different temperatures.

The phenylene–O axis has been taken to be the alignment axis of chain sequences in our analyses of D NMR. Therefore, the order parameters obtained from H NMR dipolar splittings above should coincide with those evaluated from the D NMR quadrupole splittings, if our model of nematic chain conformations for $C_{10}D_{20}$ groups is to be valid. The excellent agreement shown by the comparisons in Figure 6 therefore validates our procedure of analyzing the D NMR spectra and confirms the resultant conclusion on the nematic chain conformations described above.

Discussion

The results above demonstrate clearly that ordinarily flexible $C_{10}D_{20}$ groups assume highly extended configurations in the nematic state. This finding from the NMR investigations is therefore in agreement with the conclusion reached in I from considerations of the enthalpy and the entropy changes at the isotropic–nematic transition of this polymer. This high degree of conformational ordering is undoubtedly the most prominent feature that distinguishes polymeric nematogens from their monomeric counterparts.

The fact that the disorder–order transition of polymers involves such a high degree of conformational order is in

qualitative agreement with the theoretical predictions of lattice models. In this regard, it is to be noted that recent Monte Carlo simulations of cubic-lattice chains[16] show the ordered state of polymers to exhibit nearly perfect order in both conformation and orientation, in good agreement with the predictions of mean-field theory.[17] In quantitative comparisons, however, we find that the nematic conformations illustrated in Figure 1 still retain a considerable amount of gauche conformations. This seems to be related to the geometrical features of poly(methylene) chains which cannot be represented well by the cubic lattices and thus points out the limitations of ideal models in representing the diverse configurations exhibited by real chains. Hence, it is most likely that the conformational order in real polymers will depend strongly on the details of their geometrical and configurational characteristics. Nevertheless, the strong preference for highly extended conformers is expected to be a general feature.

The orientational order parameters of the nematic state observed here, falling between 0.75 and 0.85, are in close agreement with the results of Martins et al.,[3] who carried out H NMR measurements on a similar polymer system, but without deuterium labeling. The value of the order parameter at the transition, $s_{NI} \approx 0.75$, is somewhat larger than the previous estimate on this polymer, $s_{NI} \sim 0.60$, which was determined from measurements of diamagnetic anisotropy in the nematic state.[4] This difference seems to be due to the higher molecular weight of the sample used in the latter measurements; it is most likely that the applied field was not high enough to obtain complete alignment of nematic domains of the higher molecular weight samples. Alternatively, the presence of isotropic phase coexisting with the nematic state will also lead to a lower estimate from the measurements that average over the entire sample, e.g., diamagnetic anisotropy,[2,4] IR dichroism,[6] etc. In this regard, the NMR methods are preferred due to the natural separation of signals from the isotropic phase that may coexist with the anisotropic phase as well as the anisotropic domains that are not aligned properly.

In the nematic temperature ranges studied here, our sample contains both nematic and isotropic phases of varying proportions; at 193 °C the nematic portion comprises approximately half of the sample. However, as long as NMR measurements can separate the signals from the two phases, the mere presence of the coexisting isotropic phase should bear little significance for our express purpose of investigating the chain ordering in the nematic state. Moreover, since the chains of relatively lower molecular weights are most likely to be concentrated in the isotropic phase, the nematic phase of our sample may be taken to represent the characteristics of reasonably high molecular weight systems.

The value of the order parameter at the transition, $s_{NI} \approx 0.75$, is quite high but still departs considerably from the nearly perfect order predicted by lattice models. It is also at the upper limit of the predictions of wormlike chain models.[18] This result may be related to the fact that real chain conformations exhibit departures from the strictly lattice-like character owing to the appreciable range, ca. 20°, in the allowed torsional angles around each rotational isomeric state of poly(methylene) chains.[19] The torsional librations thus afforded may add some wormlike character to the lattice-like nature of rotational isomeric state models. Therefore, the orientational order parameters of real polymers are also likely to depend on the details of their chain conformations.

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Registry No. $(C_{10}H_{20}OC_6H_4COOC_6H_4OC_{10}H_{20}OC_6H_4OOCC_6H_4O)_x$ (SRU), 70857-27-1; (4,4′-bis(chloroformyl)-1,10-diphenoxydecane)·(4,4′-dihydroxy-1,10-diphenoxydecane) (copolymer), 70856-66-5.

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