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Anionic Copolymerization of Elemental Sulfur with Propylene Sulfide

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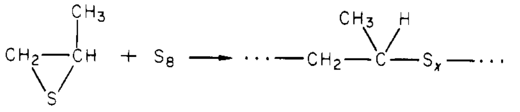
ABSTRACT: Copolymerization of elemental sulfur with propylene sulfide, initiated with sodium thiophenoxide (the sodium cation was complexed with dibenzo-18-crown-6 ether), in benzene solvent at 80 °C leads to copolymers with high sulfur content. Comparison of ^{1}H NMR spectra (60 MHz), ^{13}C NMR spectra (15, 1 MHz), laser Raman spectra, and elemental analysis results indicates that true copolymers with high sulfur contents (up to 85 wt %, i.e., with an average x in $-[CH_2CH(CH_3)S_x]-$ up to 8) are formed. The kinetics of copolymerization was studied by using ^{1}H NMR and laser Raman techniques for monitoring concentrations of monomers, i.e., of propylene sulfide and elemental sulfur, respectively. The initial rate of copolymerization decreases (with respect to both propylene sulfide and elemental sulfur comonomers) with increasing initial ratio of comonomers: [elemental sulfur]$_0$/[propylene sulfide]$_0$. Kinetic analysis allowed the ratio of the rate constants of homo- and cross-propagations to be determined. Thus the relative reactivities of sulfur vs. propylene sulfide toward the thiolate anion were found to be equal to 7.5 (without considering the statistical factor).

Introduction

We have shown recently that elemental sulfur can be copolymerized with cyclic sulfides well below the floor temperature (a thermodynamic barrier) of sulfur homopolymerization by using simple anionic initiators.[1-3] This new process leads eventually to high molecular weight polysulfides with polysulfur bridges of various lengths (x in eq 1):



(1)

Polymers with an average x as high as 8 were prepared from propylene sulfide and elemental sulfur.

In the present paper we describe the ^{1}H NMR, ^{13}C NMR, and laser Raman spectra of the prepared products as well as preliminary kinetic measurements in order to demonstrate that a true copolymerization process proceeds. Laser Raman spectra clearly indicate that there is no elemental sulfur left in the products; thus sulfur is indeed bound in the linear polysulfide bridges of the macromolecules.

Studies of the kinetics of copolymerization enabled the process to be described in terms of the usual set of ratios of homo- and cross-propagation rate constants, complemented with scrambling reactions.

Experimental Section

Materials. Elemental sulfur (S_8) (Kopalnia Siarki-Grzybów, Poland) for spectroscopy (99.999% pure) was dissolved in benzene, and the resulting solution was degassed in a high-vacuum system and stored in the dark.

Propylene sulfide (P) (Fluka AG, Chemische Fabrik) was purified as described[3] and distilled in a high-vacuum system from a sodium mirror just before use.

Sodium thiophenoxide initiator (the sodium cation was complexed with dibenzo-18-crown-6) was prepared from thiophenol and sodium metal under high-vacuum conditions.

Crown ether, dibenzo-18-crown-6, was prepared as described in ref 5 and sublimed in vacuo.

Benzene (POCh, Poland) was refluxed over sodium metal for several days and then fractionated, and the middle fraction was degassed and condensed in the vessel with liquid Na/K alloy. Reaction mixtures were prepared as we described previously.[3]

Poly(propylene pentasulfide) was obtained by reacting 1,2-dichloropropane (DCP) and sodium pentasulfide (Na_2S_5) in the presence of $CdCO_3$. DCP, an aqueous solution of Na_2S_5 (DCP/Na_2S_5 molar ratio equal to 1), and $CdCO_3$ (2% on comonomers) were poured into a three-necked round-bottom flask equipped with a stirrer and a condenser. Then the reaction mixture was vigorously stirred at the boiling temperature for several hours. The resulting polymer was then dissolved in CH_2Br_2, washed with distilled water several times, precipitated into methanol, and finally dried in vacuo.

Conversions of both S_8 and P were determined independently; thus the instantaneous concentration of P was determined by ^{1}H NMR (Perkin-Elmer, 60 MHz) and the concentration of S_8 was determined by laser Raman spectroscopy (Cary 82, Varian Raman spectrometer with an argon ion laser emitting at 5145 Å; 100-mW power in the sample, 3-cm^{-1} spectral slit width). ^{1}H NMR and Raman measurements were performed in 3-mm-i.d. Pyrex tubes sealed under vacuum.

Kinetic Measurements

Kinetics of P disappearance was followed by NMR. The ^{1}H NMR spectrum of P shows three groups of signals due to CH_3 (doublet, δ 1.39), CH_2 (two doublets, δ 2.1), and CH (sextet, δ 2.4) proton absorptions, respectively (Figure 1a). During copolymerization the intensity of the CH_2 peaks decreases and both doublets eventually disappear after conversion of P into the copolymer. New bands do not appear in this region from the copolymer formed.

Thus peak areas of this doublet at δ 2.1 were taken as a measure of the momentary concentration of P during copolymerization, and the peak area of the CH_3 peak (a sum of monomer and polymer) was applied as an internal standard.

Conversion of S_8 was determined from laser Raman spectra. Two bands of S_8 in dilute solutions are observed in the range 200–650 cm^{-1}, namely, at 217 and 475 cm^{-1} (Figure 2). Intensities of both signals (217 and 475 cm^{-1}) decrease with progress of the copolymerization. In the range 400–550 cm^{-1} new bands appear, however, due to the S–S stretching vibrations in the polysulfide linkages in the copolymers formed (Figure 2b,c). Fortunately, in the region close to 217 cm^{-1} new bands do not arise; therefore the intensity of the band at 217 cm^{-1} has been used throughout this work.

Benzene (scattering at 607 cm^{-1}) was used as an internal standard. The momentary concentration of S_8 was evaluated from the surface area under the band at 217 cm^{-1} and from the experimental dependence $8[S_8] = 7.7 \times 10^{-2}[C_6H_6](S_{217}/S_{607})$ (where S_{217} and S_{607} denote the surface areas under the bands at 217 and 607 cm^{-1}, respectively).

In order to determine the corresponding reactivities, copolymerizations with various ratios of starting concentrations of monomers, $[S_8]_0/[P]_0$, were used (Figures 3 and 4).

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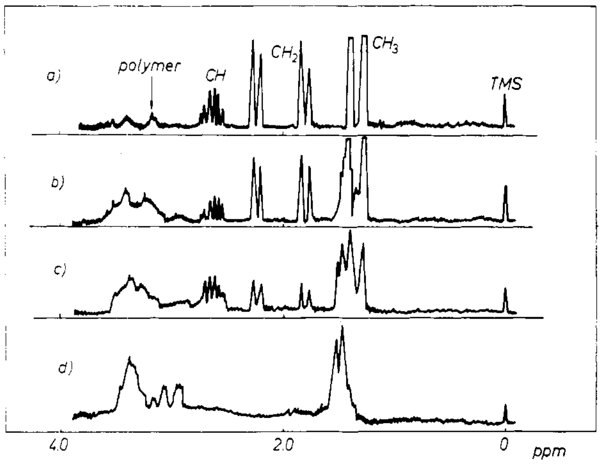


Figure 1. ^1H NMR spectra (60 MHz) of (a) propylene sulfide monomer (P) (0.8 mol/L in C_6H_6 solution), (b,c) mixtures of copolymer and P monomer during copolymerization, and (d) copolymer of P with S_8. Conditions of copolymerization: $[P]_0 = 0.8$ mol/L, $8[S_8]_0 = 2$ mol/L, $[I]_0 = 10^{-3}$ mol/L, solvent = C_6H_6, $t = 80$ °C.

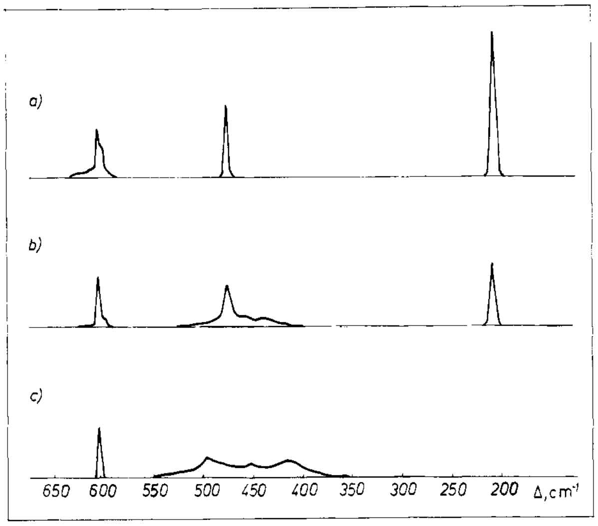


Figure 2. Raman spectra of P-S_8 reaction mixtures: (a) at the start of copolymerization ($t = 0$); (b) during copolymerization ($t = 50$ min); (c) spectra of P-S_8 copolymer. (Conditions of copolymerization as in Figure 1.)

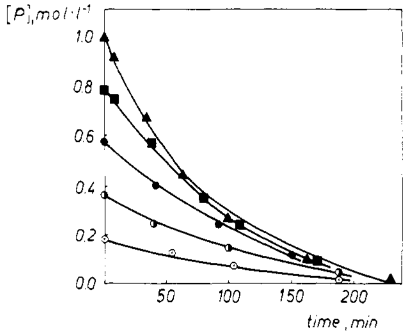


Figure 3. [P] = $f(t)$ kinetic curves. Conditions of copolymerization: $8[S_8]_0 = 2$ mol/L, $[I]_0 = 10^{-3}$ mol/L, solvent = C_6H_6, $t = 80$ °C. $[P]_0$: (▲) 1, (■) 0.8, (●) 0.6, (◑) 0.4, and (○) 0.2 mol/L.

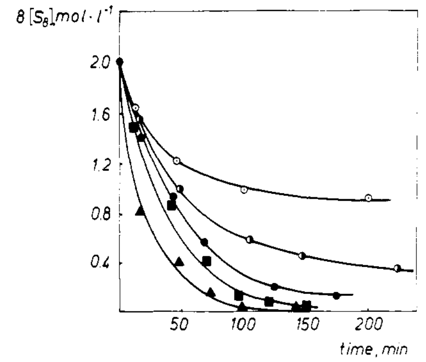


Figure 4. $[S_8] = f(t)$ kinetic curves (conditions as in Figure 3).

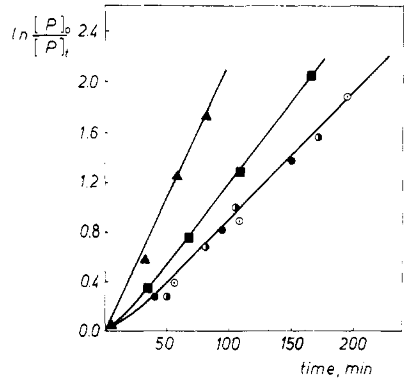


Figure 5. Semilogarithmic representations of kinetic curves: ln $\{[P]_0/[P]_t\} = f(t)$ (conditions as in Figure 3).

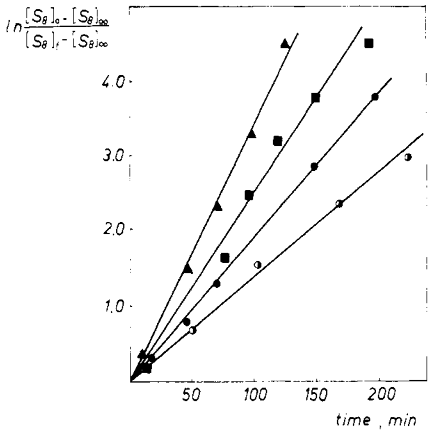
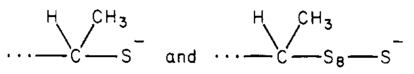


Figure 6. Semilogarithmic representations of kinetics curves: ln $\{([S_8]_0 - [S_8]_\infty)/([S_8]_t - [S_8]_\infty)\} = f(t)$ (conditions as in Figure 3).

The concentration of initiator was constant and equal to 10^{-3} mol/L. Linearity of semilogarithmic plots of $[S_8]$ and [P] against time strongly indicates that the concentration of active species does not change during copolymerization (Figures 5 and 6). Semilogarithmic plots of S_8 are linear only for the high starting concentration of S_8 and/or high starting concentration of P. The higher the starting concentration of P, the higher the proportion of S_8 incorporated into the copolymer and the lower its "equilibrium" concentration. This problem will be discussed in more detail elsewhere.

Preliminary analysis of the ^{13}C spectra shows (cf. next section) that copolymers isolated at high conversions do not merely consist of $-S_1-$ and $-S_9-$ units, as could be assumed if only homo- and cross-propagation reactions are taken into account. Thus another process should be considered which leads to the statistical distribution of polysulfide bridge lengths. Since it is known that the thiophilic displacement at sulfur proceeds faster for linear polysulfides (except disulfides) than for elemental sulfur (*cyclo*-octasulfur), we have to assume that this is a scrambling process, responsible for the fast equilibration of the polysulfur bridges.

Nevertheless, for the treatment of the kinetics of copolymerization we tentatively assume that the actual copolymerization process proceeds on only two active species, namely



$\cdots\!-\!\mathrm{C(H)(CH_3)}\!-\!S^-$ and $\cdots\!-\!\mathrm{C(H)(CH_3)}\!-\!S_8\!-\!S^-$

This is indeed possible at low conversions, when the rate of scrambling is low, due to the low concentration of copolymer relative to monomer.

Thus the kinetic scheme can be described in terms of a usual set of homo- and cross-propagation reactions:

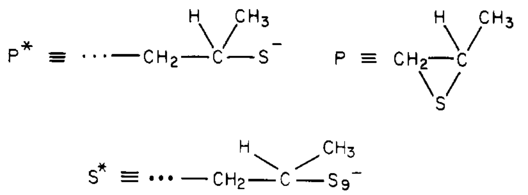
$$P^* + P \xrightarrow{k_{pp}} P^* \qquad (2a)$$

$$P^* + S_8 \underset{k_{-ps}}{\overset{k_{ps}}{\rightleftharpoons}} S^* \qquad (2b)$$

$$S^* + P \xrightarrow{k_{sp}} P^* \qquad (2c)$$

$$S^* + S_8 \underset{k_{-ss}}{\overset{k_{ss}}{\rightleftharpoons}} S^* \qquad (2d)$$

where



$P^* \equiv \cdots\!-\!CH_2\!-\!\mathrm{C(H)(CH_3)}\!-\!S^-$ $\quad P \equiv CH_2\!-\!\mathrm{C(H)(CH_3)}$ (with S bridging) $\quad S^* \equiv \cdots\!-\!CH_2\!-\!\mathrm{C(H)(CH_3)}\!-\!S_9^-$

The reaction with rate constant k_{ss} (eq 2d) does not need to be taken into account because below the floor temperature for S_8 homopolymerization (159 °C) the equilibrium would be shifted to the left-hand side almost completely.

Thus we can write the corresponding set of differential equations related to this kinetic scheme:

$$\frac{d[P]}{dt} = -k_{pp}[P^*][P] - k_{sp}[S^*][P] \qquad (3a)$$

$$\frac{d[S_8]}{dt} = -k_{ps}[P^*][S_8] + k_{-ps}[S^*] \qquad (3b)$$

and

$$\frac{d[P^*]}{dt} = -k_{ps}[P^*][S_8] + k_{-ps}[S^*] + k_{sp}[S^*][P] = 0 \qquad (4a)$$

$$\frac{d[S^*]}{dt} = k_{ps}[P^*][S_8] - k_{-ps}[S^*] - k_{sp}[S^*][P] = 0 \qquad (4b)$$

Simultaneous solution of eq 3a,b and 4a,b leads to the following final equation:

$$\frac{[S_8]}{[P]}\left(\frac{d[P]}{d[S_8]} - 1\right) = r + r\rho\frac{1}{[P]} \qquad (5)$$

where $r = k_{pp}/k_{ps}$, $\rho = k_{-ps}/k_{sp}$, and $[S_8]$ and $[P]$ denote the concentrations of elemental sulfur and propylene sulfide, respectively.

Employing the kinetic curves for $[S_8]$ and $[P]$ (Figures 3 and 4), we obtained the linear dependence of $([S_8]/[P])(d[P]/d[S_8] - 1)$ vs. $1/[P]$, from which numerical values for r and ρ were determined (Figure 7).

$$r = 1.34 \times 10^{-1} \qquad \rho = 8.65 \times 10^{-3}\ \mathrm{mol}$$

Thus $k_{ps}/k_{pp} = 7.5$ and $k_{sp}/k_{-ps} = 117\ \mathrm{mol}^{-1}$. These values reflect the high efficiency of the copolymerization of P with S_8. When reactions of S_8 are compared with other compounds, one has to remember that the statistical factor for sulfur is equal to 8.

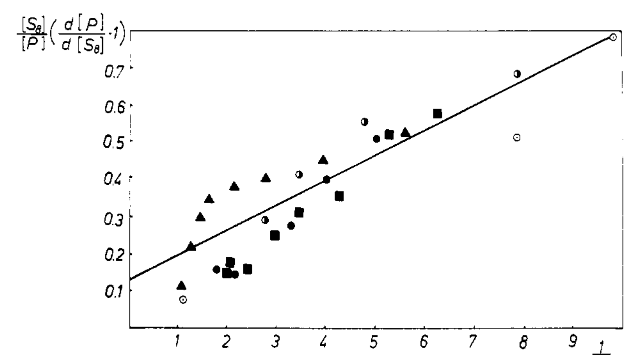


Figure 7. Plot of $([S_8]/[P])(d[P]/d[S_8] - 1)$ vs. $1/[P]$. $8[S_8]_0/[P]_0$: (▲) 2; (■) 2.5; (●) 3.33; (◑) 5.0; (○) 10.

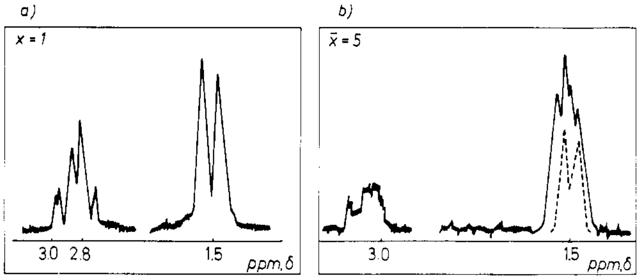


Figure 8. ^{1}H NMR spectra (60 MHz) of polysulfide polymers $-(CH_2CH(CH_3)S_x)_n-$: (a) $\bar{x} = 1$ (homopolymer of P); (b) $\bar{x} = 5$ (P–S_8 copolymer). 10 wt % solutions in o-dichlorobenzene, t = 35 °C.

^{1}H NMR, ^{13}C NMR, and Laser Raman Spectra of Copolymers

The description of the spectra in this section does not attempt to give at present detailed information about the microstructure of copolymers (tacticity, distribution of polysulfide bridge lengths, etc.). We merely describe the spectra, with the aim of showing that the obtained products are true copolymers. This is important because elemental sulfur is also known to be capable of giving solid solutions with polysulfides and related compounds.

Figure 8 shows a comparison of the ^{1}H NMR spectra of the homopolymer ($x = 1$) and the copolymer of P with S_8 ($\bar{x} = 5$); chemical shifts of all groups of protons (CH_3, CH_2, CH) are shifted downfield in the copolymer. The methyl proton multiplet seems to be due to the overlapping of two doublets, the first due to the homoblocks of P and the second (downfield) due to the blocks of propylene units separated by polysulfide bridges.

It is known that the chemical shifts in dialkyl polysulfides slightly depend on the number of sulfur atoms in the polysulfide bridge. The longer the polysulfide bridge, the more downfield shifted is the proton absorption.[6]

The ^{13}C NMR spectra of the P homopolymer (Figure 9a) and the copolymers (Figure 9b–d) with an average composition $-(CH_2CH(CH_3)S_x)_n-$ (where $\bar{x}$ = 1.3, 2.0, and 5.0) clearly show that the copolymers are composed of P dyads and P units separated by more than one sulfur atom.

Sigwalt et al.[7] have shown that the ^{13}C NMR spectrum of the homopolymer consists of four singlets—CH_3, δ 20.7; CH_2, δ 38.3; CH, δ 40.4, 40.1 (due to the meso and racemic dyads)—but in polymers having additional -SS- linkages new signals appear: CH_3, δ 19.4; CH_2, δ 37.4; CH, δ 46.4, 46.1, 45.7, 44.4. As we can see in our case (Figure 9b–d) intensities of these additional signals, due to the polysulfur sequences, increase with increasing sulfur content. Comparison of the intensity of the signals at δ 20.7 and 19.4 for the copolymer having $\bar{x}$ = 2 (1:1) leads to the conclusion that the copolymers do not contain merely S_1 and S_9 units

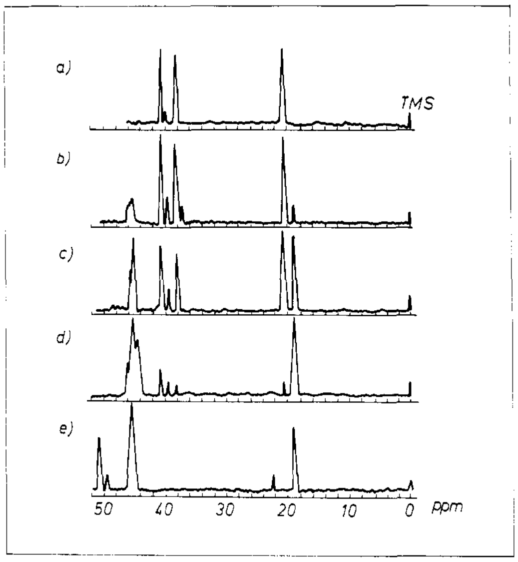


Figure 9. ^{13}C NMR spectra (15.1 MHz) of polysulfide polymers $-(CH_2CH(CH_3)S_x)_n-$: (a) $\bar{x} = 1$; (b) $\bar{x} = 1.33$; (c) $\bar{x} = 2$; (d) $\bar{x} = 5$. (e) Polycondensation product prepared from 1,2-dichloropropane and sodium pentasulfide (cf. Experimetnal Section). 10 wt % solutions in o-dichlorobenzene/C_6D_6, t = 42 °C.

because in this case the ratio of intensities should be close to 10:1. It is reasonable to assume that the NOE effect should not influence the ratio to such an extent that exclusively S_1 and S_9 units in 10:1 proportion would give a 1:1 ratio in the spectrum. Thus the observed ratio, being almost equal to 1:1, should come from scrambling reactions giving a certain distribution of polysulfide sequence lengths with apparently dominating S_1 and S_2 units. Thus eventually for $\bar{x} = 2$ the intensities for carbon atoms linked to S_1 and S_x, where $x \geq 2$, are comparable. However, due to the low-resolution conditions we cannot distinguish between the signals due to the carbon atoms separated by different numbers of sulfur atoms in the polysulfide bridges.

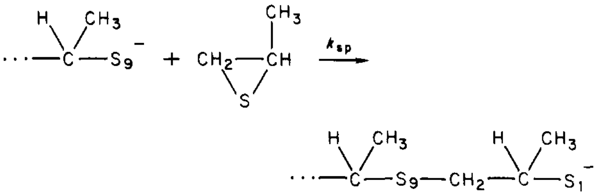
The sulfur content in the copolymers (average x) was established by elemental analysis complemented by laser Raman spectroscopy.

Copolymers for elemental analysis were prepared by exhaustive extraction with boiling methanol until the UV absorption characteristic of S_8 was no longer observed. Spectra of copolymers (e.g., Figure 2c) show exclusively bands of scattering due to the S–S vibration in linear polysulfides, but no bands due to the S_8 scattering. Thus comparison of ^{13}C NMR, laser Raman, and elemental analysis results proves that the products of reaction are true copolymers with sulfur contents up to 85 wt %. These results are particularly important because recently Aliev et al. reported that by their method and with their conditions sulfur and propylene sulfide did not form copolymers with S contents higher than that corresponding to poly(disulfide).[9,10]

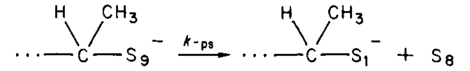
Although it is not our task to explain why others (e.g., ref 11) were not able to obtain copolymers of S_8 with longer polysulfide bridges as described in this work, we think that this is mostly a question of initial sulfur concentration and temperature of the process. As will be shown in our next paper on the thermodynamics of the copolymerization, the equilibrium concentration of S_8 in the copolymerization *decreases* with *increasing* temperature of copolymerization.

It is particularly rewarding to compare in Figure 9 the spectrum of copolymers with $\bar{x} = 5$ prepared by copolymerization (Figure 9d) with the spectrum of the polycondensation product (Figure 9e) prepared from sodium pentasulfide (Na_2S_5) and 1,2-dichloropropane (cf. Experimental Section). The spectrum of the polycondensation product contains predominantly in the high-field region a singlet at δ 19.4 due to the CH_3 carbon absorption in the field of the polysulfide bond. The origin of the small signal at δ 22.4 close to CH_3 absorption in the field of S_1 units is not clear to us at present.

The successful copolymerization of propylene sulfide with elemental sulfur is well reflected by the values of $r = k_{pp}/k_{ps}$ and $\rho = k_{-ps}/k_{sp}$. If we take into account the statistical factor (8 atoms of S in elemental sulfur susceptible to attack by an anion and only one carbon atom in propylene sulfide susceptible to the same attack), then we have almost identical reactivities of both comonomers toward the thiolate anion $\cdots-CH(CH_3)-S_1^-$. Addition of both comonomers to $\cdots-CH(CH_3)-S_9^-$ may even proceed with the same rate constants, but addition of propylene sulfide is irreversible, whereas addition of S_8 is highly reversible. This decreases the changes of S_8 to be incorporated into a copolymer. Moreover, addition of S_8 to $\cdots-S_1^-$ is also reversible and if the equilibrium is established faster than the next monomer addition to $\cdots-S_9^-$ takes place, then, again, the changes of incorporation of S_8 would be very much reduced. Fortunately, k_{sp}/k_{-ps}, i.e., the ratio of the rate constants for the two reactions



$$\cdots-CH(CH_3)-S_9^- + CH_2\!-\!CH(CH_3)\,(S) \xrightarrow{k_{sp}} \cdots-CH(CH_3)-S_9-CH_2-CH(CH_3)-S_1^- \quad (6)$$

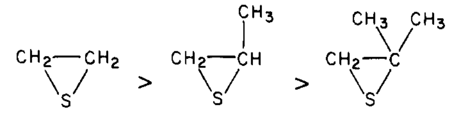


$$\cdots-CH(CH_3)-S_9^- \xrightarrow{k_{-ps}} \cdots-CH(CH_3)-S_1^- + S_8 \quad (7)$$

is high; i.e., the lifetime of $\cdots-CH(CH_3)-S_9^-$ is sufficiently high to freeze the $\cdots-S_9-\cdots$ sequence in the copolymer.

The depropagation step with the rate constant k_{-ps} is relatively slow as it follows from the determined value of ρ. This step converts the thiolate anion preceded by eight sulfur atoms into the thiolate anion preceded by one carbon atom. The former thiolate anion is much more stable; its pair of electrons interacts with empty orbitals of the preceding sulfur atoms. No stabilizing effects are possible for the thiolate anion preceded by one carbon atom.

It is difficult to discuss reasons for differences or similarities of reactivities of cyclic sulfides and elemental sulfur because these compounds react with thiolate anion by different mechanisms. It is, however, possible to determine relative reactivities of various cyclic sulfides toward thiolate anion. Sulfur affinity toward thiolate anion has to be taken as a standard and then values of r determined for various cyclic sulfides can be compared. Although numerical values of r are not yet determined for cyclic sulfides other than propylene sulfide, qualitative comparison of the copolymerization processes gives the following order of reactivities:



Both electronic and steric factors agree well with this order of nucleophilic attack on the least substituted carbon atom (CH_2) in the thiirane ring. A similar range of reactivities was observed earlier in direct studies of copolymerization.[8]

The statistical factor doubles the reactivity of ethylene sulfide.

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Annealing of Poly(vinylidene fluoride) and Formation of a Fifth Phase

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ABSTRACT: Annealing behavior in films of poly(vinylidene fluoride) containing TGT$\bar{G}$ chains in either an antipolar packing (α phase) or a polar arrangement (δ phase) has been studied. As regards the α phase, single crystals, or films isothermally drawn at high temperatures, do not undergo solid-state transformations to the γ form during annealing; defect-ridden structures or adjacent γ crystals are generally required to produce an $\alpha \rightarrow \gamma$ transformation. However, annealing of drawn α films causes changes in the diffraction pattern that imply conversion to a nonstatistically packed arrangement of α chains. The polar analogue of the α phase (δ phase) easily transforms at high temperatures to yield a mixture of polymorphs: dominant among these is the polar γ phase, while smaller amounts of its antipolar analogue (ϵ phase) and of the α phase are also formed. The previously suggested existence of this ϵ phase is demonstrated on the basis of X-ray diffraction data.

Introduction

Four crystalline polymorphs of poly(vinylidene fluoride) (PVF$_2$) have been described in the literature. The α phase is the one commonly obtained by crystallization from the melt;[1,2] its molecular chains adopt a distorted TGT$\bar{G}$ conformation and pack in a unit cell with a = 4.96 Å, b = 9.64 Å, c = 4.62 Å, and all angles = 90°.[3,4] Although each TGT$\bar{G}$ chain possesses a net dipole moment, the α-unit cell is not polar because alternate chains pack with their dipole components normal to c in an antiparallel fashion.[3,4] However, poling under a high electric field causes reversal of these dipole components in every second chain,[5,6] leading to a polar analogue of α-PVF$_2$ known as the δ phase.[7] This reversal may be accomplished by physical rotation of alternate chains through 180°[5,6] or through propagation of a 180° twist along the molecular chain;[8] however, a seemingly simpler mechanism requiring no physical rotation of chains, but only small intramolecular rotations that alter the TGT$\bar{G}$ conformation to T$\bar{G}$TG, has recently been proposed.[9] The common ferroelectric[10] phase of PVF$_2$ is the β phase, in which the molecules assume an all-trans conformation[11] (or a statistically distorted version thereof[8]) and pack in an orthorhombic unit cell with a = 8.58 Å, b = 4.91 Å, and c = 2.56 Å.[3] The fourth known polymorph of PVF$_2$ is the γ phase, which was shown by Weinhold and co-workers[12,13] to have essentially the same ab cell base as the α form but double the c-axis repeat. This conclusion has been confirmed by subsequent studies,[2,14–16] although the structure appears to be monoclinic,[15,16] rather than the originally suggested orthorhombic.[12,13]

In a recent paper[16] dealing with the structure of the γ phase, the possibility for existence of a fifth polymorph of PVF$_2$ (ϵ phase) was noted; the present study offers experimental evidence and a discussion of the conditions for manifestation of such a fifth form.

Experimental Section

The PVF$_2$ samples used were KF-1100 resin, a Kureha Chemical Industry Co., Ltd., polymer having 3.8% of inverted monomeric units ("head-to-head, tail-to-tail") as determined by ^{19}F NMR.[17] Films of this polymer, ~100 μm thick, prepared by compression molding, were uniaxially drawn at 145 °C in an Instron apparatus at a rate of ~10%/min to extension ratios of 4:1–5:1. These films were coated with Al electrodes in a vacuum evaporator and then poled for 30 min at 80 °C under an electric field of 1.2 MV/cm. These specimens were annealed under vacuum with their ends restrained in a metallic holder. To prevent melting of the original samples at the high temperatures employed, the annealing temperature was gradually raised to its final value in accordance with the following heating program: 160 °C/2 h → 165 °C/2 h → 170 °C/2 h → 175 °C/1 day → 180 °C/5–25 days. After completion of heat treatment, the specimens were examined at room temperature by X-ray diffraction and IR spectroscopy.

Results and Discussion

The changes occurring in these samples as a result of the experimental procedure are reflected in their X-ray diffraction patterns depicted in Figure 1. The drawn films are initially of the α phase, whose antipolar packing is evidenced by the presence of reflections with odd $h + k$ indices (e.g., 100, 120, 121), as seen in Figure 1a. Heat treatment of the α phase has been found[15,18] to result in a gradual change in conformation from TGT$\bar{G}$ to T$_3$GT$_3\bar{G}$. However, in the case of our drawn α specimens, no such changes were ever observed, as may be seen in Figure 1b: here, even after excessive annealing (25 days at 175 °C), neither new layer lines characteristic of the γ phase[12,13,15] nor diffuse streaks consistent with intermediate defect structures[15,19–21] are apparent (such changes in conventionally drawn α-PVF$_2$ have also been found missing in the

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