changes of statistical weight factors. Therefore, the assignment of the chemical shifts in this study was not affected by these changes.

The calculation of conformer population was carried out for poly(methyl propenyl ether) (PMPE) and poly(isopropyl propenyl ether) (PIPPE) by the same method as for PEPE. There was little difference in the main-chain conformation among PMPE, PIPPE, and PEPE. Therefore, the calculated chemical shifts of $C_{\beta 1}$ and $C_{\beta 0}$ showed almost the same tendency. The assignments for the $C_{\beta 1}$ carbons of PIPPE and PMPE are similar to that of PEPE; that is, absorptions due to erythro,meso, racemic, and threo,meso structures appear in this order from low field.

References and Notes

(1) Natta, G.; Peraldo, M.; Farina, M.; Bressan, G. *Makromol. Chem.* **1962**, *55*, 139.
(2) Natta, G. *J. Polym. Sci.* **1960**, *48*, 219.
(3) Ohsumi, Y.; Higashimura, T.; Okamura, S.; Chujo, R.; Kuroda, T. *J. Polym. Sci., Part A-1* **1967**, *5*, 3009.
(4) Higashimura, T.; Hoshino, M.; Hirokawa, Y.; Matsuzaki, K.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2691.
(5) Hirokawa, Y.; Higashimura, T.; Matsuzaki, K.; Kawamura, T.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1473.
(6) Matsuzaki, K.; Morii, H.; Kanai, T.; Fujiwara, Y. *Macromolecules*, preceding paper in this issue.
(7) Tonelli, A. E. *Macromolecules* **1978**, *11*, 565.
(8) Tonelli, A. E. *Macromolecules* **1978**, *11*, 634.
(9) Spiesecke, H.; Schneider, W. G. *J. Chem. Phys.* **1961**, *35*, 722.
(10) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984.
(11) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.
(12) Provasoli, A.; Ferro, D. R. *Macromolecules* **1977**, *10*, 874.
(13) Tonelli, A. E.; Schilling, F. C.; Starnes, W. H., Jr.; Shepherd, L.; Plitz, I. M. *Macromolecules* **1979**, *12*, 78.
(14) Tonelli, A. E. *Macromolecules* **1979**, *12*, 83.
(15) Diner, U. E.; Sweet, F.; Brown, K. *Can. J. Chem.* **1966**, *44*, 1591.
(16) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.

Proton Nuclear Magnetic Resonance Investigations on Trioxane–Dioxolane Copolymerization Initiated by 2,4,5-Trisubstituted 1,3-Dioxolan-2-ylium Salts

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ABSTRACT: Trioxane–dioxolane copolymerization initiated by 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts was directly observed by NMR spectroscopy. Formation of byproducts, i.e., trioxepane and tetroxocane, was confirmed. Intensities of signals were measured in order to obtain the basic kinetic characterization of the processes investigated. The copolymerization mechanism is discussed on the basis of the results obtained.

In our previous papers[1,2] the salts of trisubstituted dioxolane were shown to initiate the homopolymerization of trioxane. Conversion–time curves obtained differed, depending on the stereochemical structure of the initiator cation. Addition of the dioxolane comonomer (D) to trioxane (TOX) was found to influence considerably the rate of polymerization. This paper presents recent results of trioxane–dioxolane copolymerizations initiated by a series of 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts, ^1H NMR spectroscopy being used as a convenient analytical technique.

Experimental Section

A. Initiators. The cis and trans isomers of 2-isopropyl-, 2-phenyl-, and 2-styryl-4,5-dimethyl-1,3-dioxolan-2-ylium hexachloroantimonates (**1a–c**, respectively) as well as the respective hexafluoroantimonates (**2**) and hexafluoroarsenates (**3**) (see Figure 1) were synthesized from the appropriate isomers of acetals and trityl salts by the method described previously.[2,3]

B. Monomers. Industrial trioxane (TOX) was refluxed and distilled over KOH and then over Na. Dioxolane (D) (Fluka AG, Buchs SG) was refluxed and distilled over Na–K alloy. All these operations were performed in a dry nitrogen atmosphere.

C. Solvent. Methylene chloride was treated with H_2SO_4, neutralized, washed with water, dried with anhydrous Na_2SO_4, rectified over P_2O_5 on a Vigreux column, and finally dried with P_2O_5.

D. Polymerization. Initiator and the solution of comonomers were incorporated into a NMR probe under dry nitrogen. Reagents and the solvent were added to the probe, keeping the following initiator, trioxane, and dioxolane concentrations: $[I]_0 = 10^{-2}$, $[TOX]_0 = 2$, and $[D]_0 = 2$ mol/L. The spectra were recorded during the polymerization utilizing a JNM-C-60H (JEOL) spectrometer. Chemical shifts were measured with respect to CH_2Cl_2 and then related to Me_4Si, taking $\delta_{CH_2Cl_2} = 5.33$. Intensities of the signals were determined by means of a built-in electronic integrator.

E. Trioxepane Synthesis. Trioxepane (TOXEP) was obtained by heating paraformaldehyde with dioxolane in the presence of catalytic amounts of H_2SO_4.[4]

Results and Discussion

1. Interpretation of the Spectra. For an equimolar ratio of comonomers the reaction mixture was found to remain homogeneous until full conversion had been reached, which allowed direct NMR observations. Moreover, the precipitation of a solid trioxane–dioxolane copolymer, which occurred in the case of some slower runs for high conversions was found to begin close to the probe walls so that, fortunately, resolution of the spectra was not affected.

Figure 2c presents the spectrum of the copolymerization system investigated. Using both literature data and comparison with the spectrum of the mixture consisting of both the comonomers (Figure 2a) and the spectrum of the dioxolane homopolymerization system (Figure 2b), we assigned the signals of the NMR spectrum of the copolymerization system (Figure 2c). Thus, according to the literature data,[5-7] the three signals in the oxymethylene region were assigned to the three copolymeric triads: M*M*M, (E*M*M, M*M*E); and E*M*E (see Table I). Since no splitting of the oxyethylene signal was reported[5-7] for the trioxane–dioxolane copolymers, one would expect that

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Table I
Me$_4$Si-Based Chemical Shifts of the Trioxane-Dioxolane Copolymers[a]

δ					
MMM	*EMM*, *MME*	*EME*	-(OCH$_2$CH$_2$)$_{pol}$-	remarks	ref
4.82	4.73	4.65	3.65	CH_2Cl_2	authors' results
4.73	4.66	4.59	3.59	CCl_4	5
5.13	5.04	4.97	3.98	$C_2H_2Cl_4$	
4.88	4.80	4.73	3.73	$CHCl_3$	6
	4.82-4.74 (3 s)		3.73	$CDCl_3$	7

[a] *MMM* = -OCH$_2$OC*H*$_2$OCH$_2$-; *EMM*, *MME* = -OCH$_2$CH$_2$OC*H*$_2$OCH$_2$-, -OCH$_2$OC*H*$_2$OCH$_2$CH$_2$-; *EME* = -OCH$_2$CH$_2$OC*H*$_2$-OCH$_2$CH$_2$-.

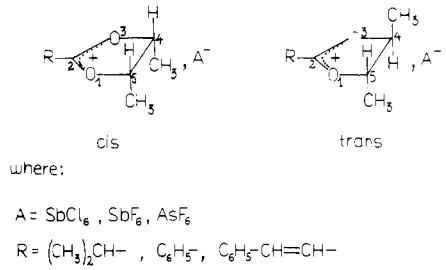

Figure 1. Structure of the initiators.

signal to exhibit the same chemical shift both in the dioxolane homopolymer and the trioxane-dioxolane copolymer. Therefore, the broadened signal at δ = 3.65 could be assigned to the poly(oxyethylene) protons.

The presence of the sharp singlet at δ = 3.72 (Figure 2c) is assumed to be the result of the formation of a certain amount of a low molecular weight compound during the copolymerization. 1,3,5-Trioxepane had been already reported to be the main byproduct in trioxane-dioxolane copolymerization.[8] Values of the chemical shifts of trioxepane given in the literature[4] (δ = 3.82 for oxyethylene protons, δ = 4.91 for oxymethylene protons) are of limited value for identification purposes since they vary considerably, depending on the measurement conditions (see Table I). Trioxepane was synthesized according to a reported procedure[4] and the spectrum of the reaction mixture obtained in CH_2Cl_2 solution was recorded. Two sharp singlets, δ = 3.72 and δ = 4.82, could be seen in this spectrum in addition to the signals of the unreacted dioxolane and the small amount of the polymeric products. Thus, the methylene signal of trioxepane overlaps with that of the *MMM* triad in the spectrum of the copolymer investigated.

When analyzing the spectra of the copolymerization system obtained at high conversion, we observed an additional signal at δ = 4.98. That low-intensity singlet can be assigned to tetroxocane (TEOX), known to be a byproduct in trioxane homopolymerization.[9] The same was also observed previously during an investigation of the homopolymerization mechanism.[2]

2. Application to Kinetics. Assuming the validity of the above-discussed interpretation of the NMR signals, we measured the intensities of the signals during the course of the polymerization in order to determine the changes in the concentrations of the particular species present in the system. Unfortunately, overlapping of the trioxepane oxymethylene signal with that of the *MMM* triad occurred and both these signals were too close to the dioxolane oxymethylene signal to allow quantitative measurement. Nevertheless, the good separation of the oxyethylene signals made possible the determination of the intensities of signals of all species present in the system under investigation since the intensities of both trioxepane signals should be equal to each other and those of dioxolane should be in a 1:2 ratio. The following abbreviations for

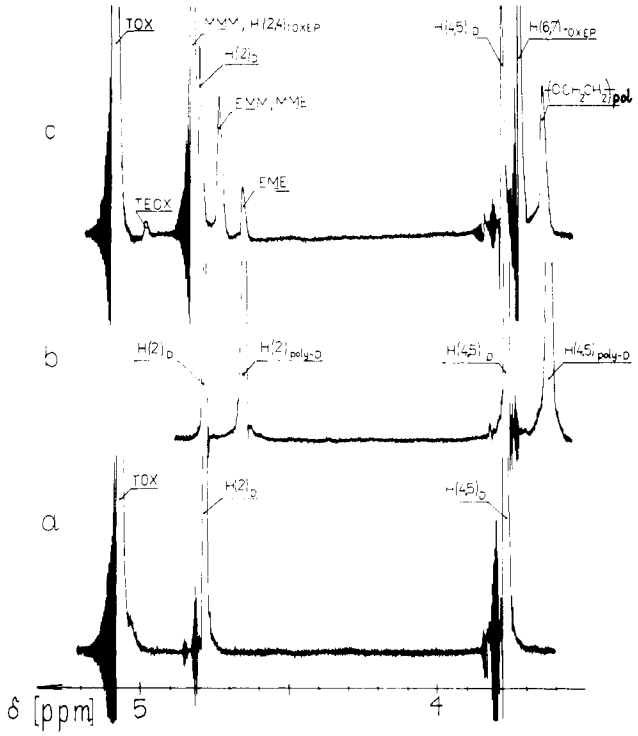

Figure 2. ^{1}H NMR spectra of the system investigated: (a) mixture of comonomers; (b) dioxolane homopolymerizing system; (c) trioxane-dioxolane copolymerizing system.

the intensities of the signals were used: *a*, trioxane; *b*, *MMM*, H(2,4) in trioxepane, H(2) in dioxolane; *c*, *MME*, *EMM*; *d*, *EME*; *e*, H(4,5) in dioxolane; *f*, H(6,7) in trioxepane; *g*, -OCH$_2$CH$_2$- in the copolymer.

It is evident that the intensity of the *MMM* signal can be expressed as $b - f - e/2$. Thus, the following equations can be derived to calculate the relative intensities of the signals of the particular species: $i_{TOX} = a/[a + b + c + d - (e + f + g)/2]$, $i_D = e/(e + f + g)$, $i_{TOXEP} = f/(e + f + g)$, $i_{-(OCH_2CH_2)_{pol}-} = g/(e + f + g)$, $i_{-(OCH_2)_{pol}-} = (b + c + d - f - e/2)/(a + b + c + d)$. These can be divided as follows: $i_{MMM} = (b - f - e/2)/(a + b + c + d)$, $i_{MME,EMM} = c/(a + b + c + d)$, $i_{EME} = d/(a + b + c + d)$.

Clearly, the values of the relative intensities are a direct measure of concentrations of particular species; e.g., for comonomers, $i_D = [D]/[D]_0$ and $i_{TOX} = [TOX]/[TOX]_0$. The actual trioxepane concentration can also be determined from the i_{TOXEP} value. For polymeric units, however, this quantitative treatment should be regarded as referring to the molar fraction of oxymethylene and oxyethylene units with respect to the total amount of oxymethylene and oxyethylene units in the system.

Plotting the calculated relative intensities against the reaction time for each initiator used, we obtained sets of curves which can be used to provide a basic kinetic characterization of the system investigated. Figure 3

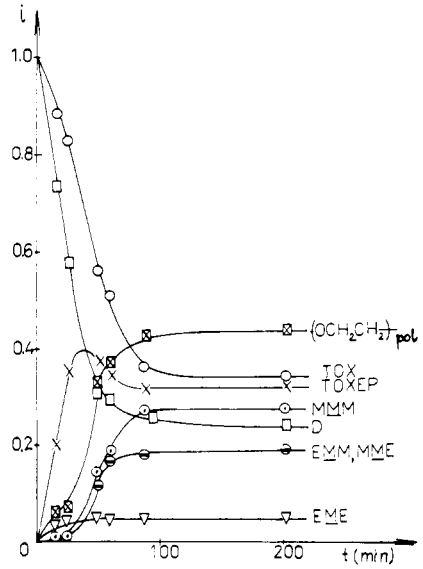

Figure 3. Changes of the relative intensities of signals in the spectra of the TOX–D copolymerizing system when initiating by *cis*-**1a** ($[TOX]_0 = 2$, $[D]_0 = 2$, $[I]_0 = 10^{-2}$ mol/L; CH_2Cl_2, room temperature).

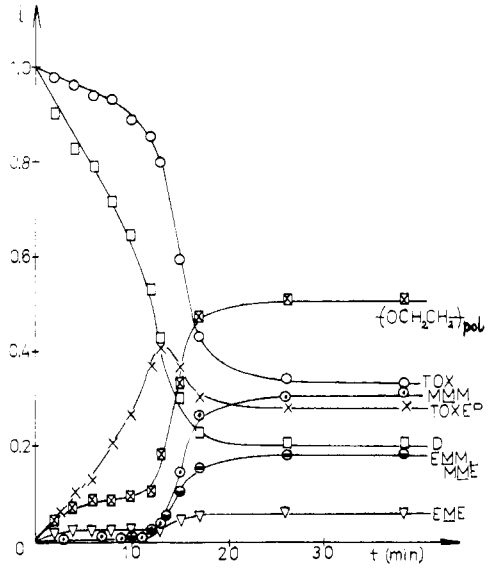

Figure 4. Changes of the relative intensities of signals in the spectra of the TOX–D copolymerizing system when initiating by *trans*-**2a** ($[TOX]_0 = 2$, $[D]_0 = 2$, $[I]_0 = 10^{-2}$ mol/L; CH_2Cl_2, room temperature).

presents results obtained with *cis*-**1a** initiation and Figure 4 with *trans*-**2a** initiation. Other initiators gave runs having a similar character.

The following molar fractions represent limiting values of the particular species as determined by their NMR intensities: $[TOX]_{lim}/[TOX]_0 = 0.34 \mp 0.02$; $[D]_{lim}/[D]_0 = 0.22 \mp 0.02$; $[TOXEP]_{lim}/[D]_0 = 0.30 \mp 0.02$; $[-(OCH_2CH_2)_{pol}-]_{lim}/[D]_0 = 0.47 \mp 0.04$; $[MMM]_{lim}/[-OCH_2-]_{total} = 0.31 \mp 0.02$; $[MME, EMM]_{lim}/[-OCH_2-]_{total} = 0.18 \mp 0.02$; $[EME]_{lim}/[-OCH_2-]_{total} = 0.05 \mp 0.02$.

The tetroxocane signal intensity did not exceed 3% of the total spectrum intensity, and it was therefore neglected in the calculations.

3. Comparison of Catalytic Activities. In order to compare differences in the catalytic activities of the several dioxolenium salts, we determined changes of the total conversion values during the polymerization, the conversion being expressed by the ratio of the sum of the signal

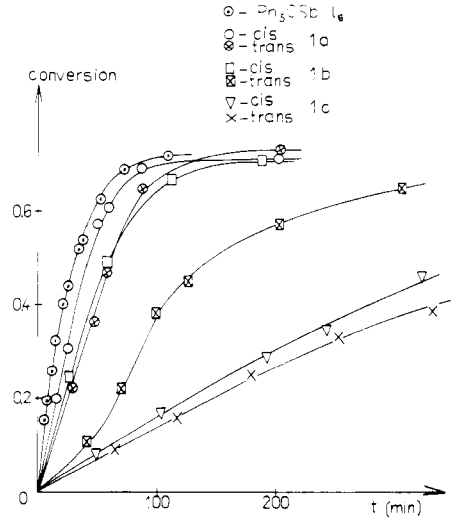

Figure 5. Conversion–time curves obtained for hexachloroantimonate salts ($[TOX]_0 = 2$, $[D]_0 = 2$, $[I]_0 = 10^{-2}$ mol/L; CH_2Cl_2, room temperature).

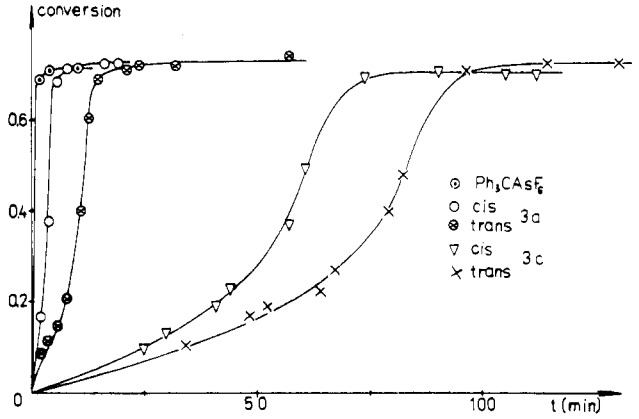

Figure 6. Conversion–time curves obtained for hexafluoroarsenate salts ($[TOX]_0 = 2$, $[D]_0 = 2$, $[I]_0 = 10^{-2}$ mol/L; CH_2Cl_2, room temperature).

intensities of the products to the total sum of the signal intensities (each comonomer possesses six protons and the same initial concentration): conversion = $(b + c + d - e/2 + f + g)/(a + b + c + d + e + f + g)$.

The conversion–time curves obtained for a series of salts previously investigated[1,2] are given in Figure 5 (hexachloroantimonates) and Figure 6 (hexafluoroarsenates). Hexafluoroantimonate salts (**2**) gave runs similar to those of **3**. Thus, **2** and **3** are more active than **1**, in accordance with previous findings.[2,10] The influence of cation structure appeared to be the same as that previously stated;[1,2,11] i.e., the salts with an alkyl group at C-2 are more active than those with an aromatic group (in particular, the styryl group) and cis isomers are always more active than the corresponding trans forms.

4. Application to Mechanism Elucidation. The comparison of the two sets of curves given in Figures 3 and 4 gives some information concerning the couse of the reactions proceeding in the system investigated. In every case three steps can be distinguished, as is seen clearly in Figure 4.

At the beginning of the first step a small and practically constant amount of the dioxolane homopolymer is formed (*EME* triad), trioxepane being simultaneously formed and its concentration increasing almost linearly to reach 40% of the initial dioxolane concentration. No copolymeric oxymethylene units are formed in that step and trioxane

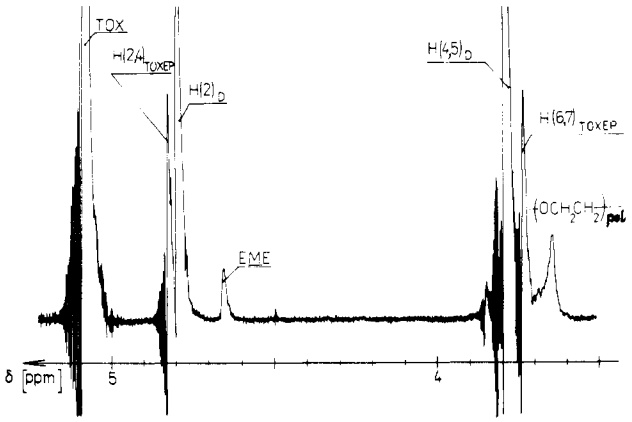

Figure 7. ^{1}H NMR spectrum of the copolymerizing system at the beginning of the process.

is used up for trioxepane formation almost exclusively.

The second step begins after trioxepane concentration has passed through its maximum. Fast formation of copolymeric oxymethylene units ((E*M*M, M*M*E) and M*M*M), an accelerated formation of poly(oxyethylene) units, and consumption of trioxane proceed simultaneously, a certain decrease of trioxepane concentration taking place. The tetroxocane signal appears after a sufficient amount of M*M*M units has been formed, and that moment can be treated as the beginning of the third step, in which concentrations of all the species present in the system approach the limiting values given above. For each initiator investigated, the limiting conversion value measured was equal to 0.72 ∓ 0.02.

The limiting conversion and concentration values may be affected by precipitation of the solid copolymer. Initially, completely soluble dioxolane homopolymer or dioxolane–rich copolymer is formed. An increase of trioxane content causes a decrease in copolymer solubility, resulting in its slow crystallization and precipitation. For slower runs this precipitation occurs just before or after the maximum conversion is reached. However, the same limiting values were obtained when very active initiators were employed. These runs were fast and therefore the system was homogeneous up to the maximum conversion. Thus, that source of measurement error can be neglected. Nevertheless, the solid copolymer precipitated slowly also in the latter case when the reaction mixture was observed after a certain period of time. For this reason, the system investiated cannot be regarded as being in a "stationary state";[4,12] the term "quasi-stationary state" should be introduced.

Some differences could be noticed when the runs obtained for different anions were compared. The curves for "stable"[10] SbF_6^- and AsF_6^- anions (Figures 4 and 6) are distinctly S-shaped when compared with those for $SbCl_6^-$ (Figures 3 and 5) anion. Similar differences resulting from the different nature of the anion have been reported for dioxolane homopolymerization initiated by tritylium salts.[13] The same differences were observed in our case for trisubstituted dioxolenium salts in the homopolymerization of dioxolane[11] but not for the homopolymerization of trioxane.[2] Moreover, independently of anion nature, tritylium salts are always more active in initiating the copolymerization than the dioxolenium ones (Figures 5 and 6). Such behavior is similar to that of dioxolane homopolymerization[11] and quite different from that of trioxane homopolymerization.[2]

The above observations may suggest that the copolymerization initiation mechanism involves mainly the reaction of initiator with the dioxolane comonomer. The NMR spectra confirm this conclusion. At the beginning of the process, the first polymeric signals are those of dioxolane homopolymeric units (Figure 7). Furthermore, the spectrum of the model system consisting of trioxane, dioxolane, and initiator exhibits signals at the initiation step similar to those observed for dioxolane homopolymerization.[14] Those signals were not seen in the case of trioxane homopolymerization.[2] Furthermore, homogenity of the copolymerization system proves that homopolymerization of trioxane is insignificant. Thus, dioxolenium salts investigated appeared to be more reactive with respect to dioxolane when compared with the trioxane comonomer. Nevertheless, final conclusions cannot be drawn before the mechanism of dioxolane polymerization initiated by the salts investigated is known.

References and Notes

(1) Gibas, M.; Jedliński, Z. *Pol. J. Chem.* **1978**, *52*, 435.
(2) Jedliński, Z.; Gibas, M. *Macromolecules* **1980**, *13*, 1700.
(3) Jedliński, Z.; Lukaszczyk, J.; Dudek, J.; Gibas, M. *Macromolecules* **1976**, *9*, 622.
(4) Schulz, R. C.; Albrecht, K.; Reutsch, C.; Tran Thi, Q. V. *ACS Symp. Ser.* **1977**, *No. 59*, 77.
(5) Opitz, G. *Plaste Kautsch.* **1975**, 951.
(6) Yamashita, Y.; Asakura, T.; Okada, M.; Ito, K. *Makromol. Chem.* **1969**, *129*, 1.
(7) Fleischer, D.; Schulz, R. C. *Makromol. Chem.* **1972**, *152*, 311.
(8) Miki, T.; Higashimura, T.; Okamura, S. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 583.
(9) Miki, T.; Higashimura, T.; Hayashi, K.; Okamura, S. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 65.
(10) Penczek, S. *Makromol. Chem.* **1974**, *175*, 1217.
(11) Jedliński, Z.; Lukaszczyk, J.; Ogórek, J. *Polym. Bull.* **1980**, *2*, 599.
(12) Szwarc, M., private communication.
(13) Plechova, O. A.; Ivanov, V. V.; Prokofeva, T. I.; Oleynik, E. F.; Enikolopyan, N. S. *Vysokomol. Soedin., Ser. A* **1973**, *15*, 14.
(14) Jedliński, Z.; Gibas, M.; Lukaszczyk, J.; Ogórek, J., in preparation.