Macromolecules **1986,** *19,* 2689–2692

The ϵ parameters describe the contact energies between the respective pairs of segments. In the case of copolymer mixtures each ϵ_{ij} has to be understood as the mean contact energy between the copolymers i and j (the other parameters, s and v^*, denote the coordination number and the hard-core segment volume, respectively).

In the case of interest, mixtures of polystyrene (segments A) and copolymers with a fraction x of brominated segments (B), the ϵ parameters become

$$\epsilon_{11} = \epsilon_{AA}$$

$$\epsilon_{22} = x^2\epsilon_{BB} + 2x(1 - x)\epsilon_{AB} + (1 - x)^2\epsilon_{AA}$$

$$\epsilon_{12} = (1 - x)\epsilon_{AA} + x\epsilon_{AB}$$

where ϵ_{AA}, ϵ_{AB}, and ϵ_{BB} denote the contact energies between styrene–styrene, styrene–bromostyrene, and bromostyrene–bromostyrene segment pairs. Insertion of these expressions results in

$$X_{12} = \frac{s}{2v^*}x^2(\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB})$$

or

$$X_{12} = x^2X_{AB}$$

with

$$X_{AB} = \frac{s}{2v^*}(\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB})$$

The second parameter, τ_{12}, appearing in eq 4 has been introduced by Patterson[13] to specify the dissimilarity in thermal expansion, that is, in free volume between the two polymeric components. It is defined as

$$\tau_{12} = 1 - T_1^*/T_2^*$$

where T_1^* and T_2^* denote the reduction temperatures of the two components to be used with the scaled equation of state. Assuming

$$T_2^* - T_1^* \approx x(T_B^* - T_A^*)$$

where T_A^* and T_B^* denote the reduction temperatures of polystyrene and polybromostyrene, gives

$$\tau_{12} \approx x\tau_{AB}$$

with

$$\tau_{AB} = 1 - T_A^*/T_B^*$$

Registry No. PS, 9003-53-6.

References and Notes

(1) McMaster, L. P. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1974,** *15,* 254.
(2) Nishi, T.; Wang, T. T.; Kwei, T. K. *Macromolecules* **1975,** *8,* 227.
(3) Casper, R.; Morbitzer, L. *Angew. Makromol. Chem.* **1977,** *58/59,* 1.
(4) Roerdink, E.; Challa, G. *Polymer* **1980,** *21,* 1161.
(5) Walsh, D. J.; Higgins, J. S.; Zhikuan, C. *Polymer* **1982,** *23,* 336.
(6) Ougizawa, T.; Inoue, T.; Kammer, H. W. *Macromolecules* **1985,** *18,* 2089.
(7) Roe, R. J.; Zin, W.-C. *Macromolecules* **1980,** *13,* 1221.
(8) Kambour, R. P.; Bendler, J. T. *Macromolecules,* preceding paper in this issue.
(9) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983,** *16,* 753.
(10) Couchman, P. R. *Macromolecules* **1978,** *11,* 1156.
(11) Malhotra, S. L.; Lessard, P.; Blanchard, L. *J. Macromol. Sci., Chem.* **1981,** *15,* 279.
(12) Paul, D. R.; Newman, S., Eds. *Polymer Blends*; Academic: New York, 1978; Vol. 1, Chapters 1–3.
(13) Patterson, D.; Robard, A. *Macromolecules* **1978,** *11,* 690.
(14) Koningsveld, R. Ph.D. Thesis, University of Leiden, 1961.
(15) Flory, P. J. *Discuss. Faraday Soc.* **1970,** *49,* 7.

Separation and Characterization of Cyclic Sulfides Formed in the Polycondensation of Dibromoalkanes with Aliphatic Dithiols

G. Montaudo,*† C. Puglisi,‡ E. Scamporrino,† and D. Vitalini‡

Dipartimento di Scienze Chimiche, Università di Catania, 95125 Catania, Italy, and Istituto per la Chimica e la Tecnologia dei Materiali Polimerici, Consiglio Nazionale delle Ricerche, 95125 Catania, Italy. *Received March 6, 1986*

ABSTRACT: Mass spectrometric and gel permeation chromatographic analyses are used to identify the cyclic oligomers formed in the polycondensation reactions of dithiols and dibromoalkanes leading to aliphatic polysulfides. A correlation exists between the two sets of data obtained by these techniques. Cyclic oligomers with only an even number of repeating units are detected among the polycondensation reaction products. This fact is considered evidence that these oligomers are generated directly from the reacting monomers and not by degradation of the corresponding polymers.

Introduction

The formation of cyclic oligomers in polycondensation reactions is a phenomenon frequently observed.[1–3]

Current methods of detecting oligomers contained in polymer samples are based on gas, liquid, and size exclusion chromatography, combined with some structural identification methods. These techniques are indeed powerful, but sometimes low volatility of samples, low solubility in suitable organic solvents, or low resolution in liquid chromatography make alternative and rapid methods of detection and identification of complex mixtures of low molecular weight compounds highly desirable.

Mass spectrometry (MS) is particularly suitable for the detection of these materials since they are volatile under high vacuum at relatively mild temperatures at which polymers remain undecomposed and therefore undetected.[4–6]

We have been interested in the synthesis and characterization of a series of polysulfides: $-((CH_2)_6S)_n-$, poly(hexamethylene sulfide) (I); $-((CH_2)_3S)_n-$, poly(trimethylene sulfide) (II); $-((CH_2)_2S)_n-$, poly(ethylene sulfide) (III); and $-(CH_2S)_n-$, poly(methylene sulfide) (IV). These

---

† Università di Catania.

‡ Istituto per la Chimica e la Tecnologia dei Materiali Polimerici.

0024-9297/86/2219-2689$01.50/0

polymers are obtained from the polycondensation of dibromoalkanes with dithiols, and gel permeation chromatography (GPC) and MS have been used to detect and identify the cyclic oligomers formed in the polymerization reactions. Several of these cyclic materials have been obtained through high-dilution reaction conditions,[7-10] but it is of general interest to determine the distribution of cyclic oligomers generated during polymerization conditions.[2,3]

Our study is aimed at comparing the distribution of cyclic oligomers detected by two methods (GPC and MS) and exploring the utility of the MS technique for the detection and characterization of oligomers contained in polymeric samples.

Experimental Section

Polymer Synthesis and Oligomer Extraction. Poly(hexamethylene sulfide) (I), poly(trimethylene sulfide) (II), and poly(ethylene sulfide) (III) were synthesized from the corresponding dithiols and dibromides according to the method described by Marvel et al.[11] In a typical procedure, 0.84 g (0.035 mol) of Na was dissolved in 25 mL of absolute ethanol. 1,6-Hexamethylenedithiol (2.58 g, 0.0172 mol) was then added, and the solution was heated. To the resulting boiling solution were added benzene (45 mL) and 1,6-dibromohexane (4.20 g, 0.0172 mol). After the vigorous and spontaneous reaction subsided, 45 mL of benzene was added, and the mixture was refluxed overnight. After the mixture cooled, it was filtered. The solution was evaporated in vacuo to yield a white powder. MS and GPC analysis showed that the recovered white powder consists mainly of cyclic oligomers. The residue, which consisted of polymer and NaBr, was repetitively washed with water. This was then dried under vaccum and dissolved in hot *N*-methylpyrrolidone (NMP). A white powder was recovered after freezer cooling.

Poly(methylene sulfide) (IV) was synthesized from $Na_2S \cdot 9H_2O$ and CH_2Cl_2 as reported in the literature.[7] Because there does not exist a solvent for both the polymer and the low molecular weight cyclic oligomers, it was impossible to analyze the reaction product by GPC. Therefore the analysis of low molecular weight compounds was accomplished by MS.

GPC Analysis. A Waters 6000A apparatus equipped with four μStyragel columns (in the order 1000-, 500-, 10 000-, and 100-Å pore size) was used. A Model R 401 differential refractometer from Waters was used as the detector. The analyses were performed at 25 °C in toluene and tetrahydrofuran (THF) at a flow rate of 1 mL/min.

Mass Spectrometry. Mass spectra were obtained on a Kratos MS 50S double-focusing mass spectrometer equipped with an Eclipse/120 data system from Data General running under DS 55 Kratos software. MS analysis was carried out by the direct insertion probe for solid materials heated from 30 to 400 °C at heating rate of 10 °C/min by the method described elsewhere.[4] Electron impact (EI) mass spectra were obtained at 18 eV. Chemical ionization (CI) was performed with ammonia (99.998%) as reagent gas, purchased from Matheson Gas Products.

Viscometry. Inherent viscosities of the experimental polymers ($\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g/dL) were measured in a Desreux–Bishoff suspended-level viscometer that contained a coarse sintered-glass filter attached just below the reservoir through which the solution passes as it rises into the capillary. The measurements were performed on purified polymers (see above) in NMP at 80 °C. The values are as follows: polymer I, $\eta_{inh} = 0.25$; polymer II, $\eta_{inh} = 0.13$; polymer III, $\eta_{inh} = 0.15$; polymer IV, insoluble.

Results

Cyclic Oligomers Formed in the Synthesis of Polymer I. The GPC trace reported in Figure 1A shows that the soluble material extracted from the crude sample of polymer I contains a series of low molecular weight compounds. The detection and identification of these compounds were achieved by introducing the extracted material into the ion source of the MS using the direct insertion probe for solid samples. The probe temperature was then gradually increased on a linear program, and the evolving products were analyzed by repetitive mass scans. A heating rate of 10 °C/min was found adequate to permit the best time–temperature resolution of the mixture. The total ion current (TIC) curve obtained for the extracted material from polymer I is reported in Figure 1B. Figure 2 shows three mass spectra recorded at temperatures corresponding to the TIC maxima observed in Figure 1B. In all three cases intense peaks corresponding to molecular ions of cyclic hexamethylene sulfide oligomers appear.

In Figure 2a, the peak at *m/z* 232 (base peak) corresponds to cyclic dimer; the peak at *m/z* 199 arises from the parent ion at *m/z* 232 after SH (*m/z* 33) loss. This transition is substantiated by a metastable peak at *m/z*

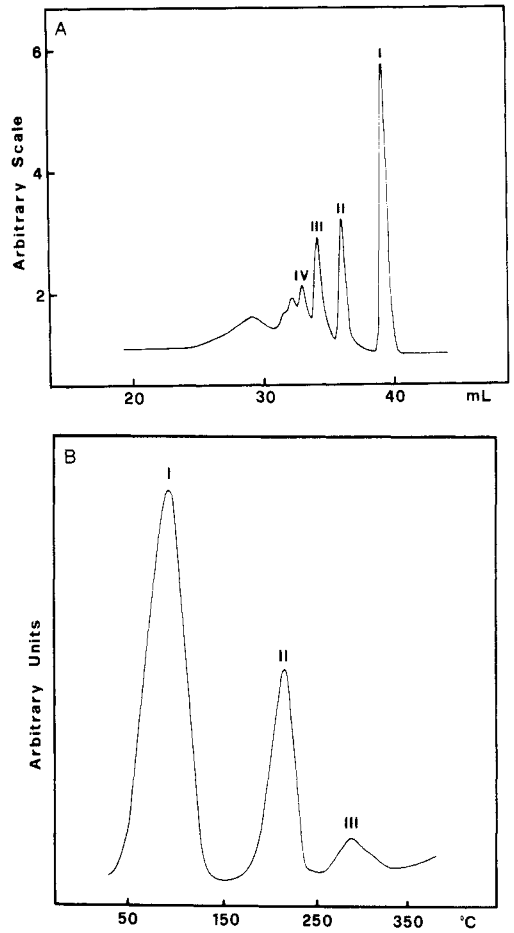

Figure 1. (A) GPC trace (toluene) and (B) MS total ion current (TIC) of the extracted material from the crude sample of polymer I: peak I, dimer; peak II, tetramer; peak III, hexamer; peak IV, octamer.

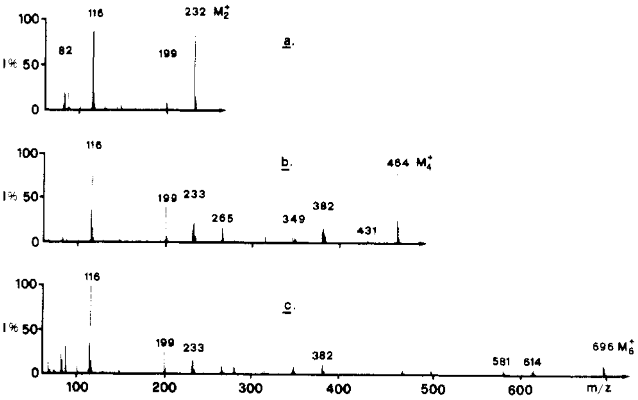

Figure 2. EI mass spectra corresponding to the three cyclic oligomers of polymer I: (a) dimer; (b) tetramer; (c) hexamer.

Table I
Cyclic Oligomers Detected in the Synthesis of Polymers I-IV

cyclic compound formula	method of detection	no. of repeating units in the cyclic oligomers 2	3	4	5	6	7	8	9	10	11	12	13	14
$[(\mathrm{CH}_2)_6\mathrm{S}]_n$ (116)^a	MS	X		X		X								
	GPC	X		X		X		X		X		X		
$[(\mathrm{CH}_2)_3\mathrm{S}]_n$ (74)^a	MS	X		X		X		X						
	GPC	X		X		X		X		X		X		X
$[(\mathrm{CH}_2)_2\mathrm{S}]_n$ (60)^a	MS	X												
	GPC	X												
$[\mathrm{CH}_2\mathrm{S}]_n$ (46)^a	MS	X	X	X	X									
	GPC													

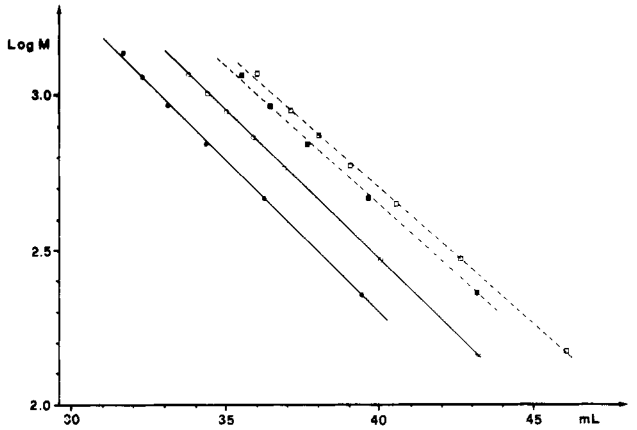

Figure 3. Dependence of the elution volume on log M of the cyclic oligomers: (—) toluene; (---) THF; (●, ■) polymer I; (○, □) polymer II.

170.7. A fragment ion at m/z 116 also appears with high intensity in the spectrum and corresponds to the splitting of the cyclic dimer in two halves. In Figure 2b, the peak at m/z 464 corresponds to cyclic tetramer. as in the previous case the EI loss of m/z 33 from the molecular ion to generate the peak at m/z 431 also occurs. However, the base peak in the spectrum appears at m/z 116. The peak at m/z 382 generated from the parent ion at m/z 464 after C_6H_8 (m/z 82) loss is also present in the spectrum. This transition is substantiated by a metastable peak at m/z 314.5.

Essentially the same features are seen in the spectrum in Figure 2c, which shows a peak at m/z 696, assigned to the molecular ion of the cyclic hexamer.

The GPC trace (Figure 1A) shows six well-separated peaks, whereas only three cyclic oligomers were detected by MS because the thermal decomposition of higher oligomers occurs before their volatilization.

However, the linear dependence of elution volume on log M (Figure 3) shows that the peaks in Figure 1A are due to oligomeric members of the same homologous series. It can be noted that only cyclic oligomers with even repeating units are detected (Table I).

In order to estimate the reliability of the cycle distribution obtained by MS, the mass spectral intensity of the three cyclic oligomers (dimer, tetramer, and hexamer) at the corresponding TIC maxima (Figure 1B) have been compared with the intensities of the corresponding three GPC peaks (Figure 1A). Figure 4 shows the correlation obtained between the two sets of data.

Cyclic Oligomers Formed in the Synthesis of Polymer II. The GPC trace in Figure 5A also shows that the soluble material extracted from the crude sample of polymer II contains a series of oligomers. Figure 5B reports the TIC curves vs. temperature for the material extracted from the crude sample of polymer II.

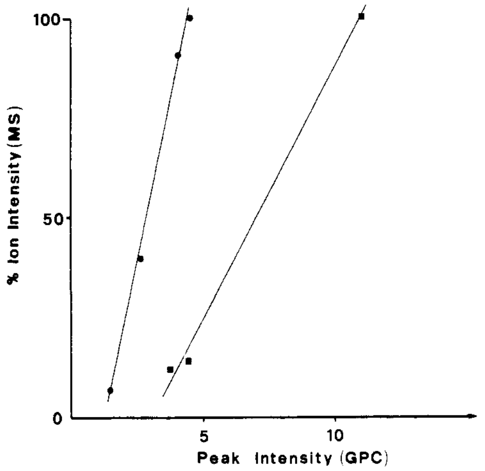

Figure 4. Percent ion intensity (MS) vs. peak intensity (GPC) of the cyclic oligomers detected for (■) polymer I and (●) polymer II.

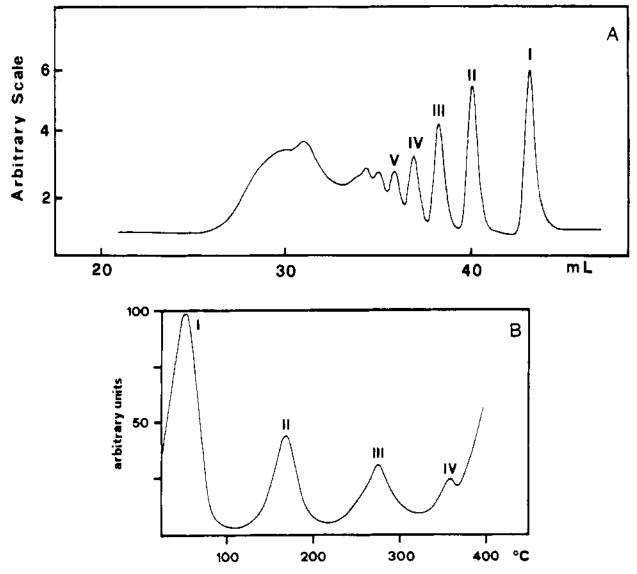

Figure 5. (A) GPC trace (toluene) and (B) MS total ion current (TIC) of the extracted material from the crude sample of polymer II: peak I, dimer; peak II, tetramer; peak III, hexamer; peak IV, octamer; peak V, decamer.

In Figure 6 the ammonia CI mass spectra corresponding to the temperature of maximum evolution rate of the four oligomers detected are reported. The spectra show peaks corresponding to the $(MH)^+$ ions of the cyclic sulfides at m/z 149, 297, 445, and 593, respectively. Chemical ionization was preferred in this case because the stability of higher oligomers to EI is low, so that molecular ions became weak in the EI spectra. Also in this case a correlation exists between GPC and MS intensities (Figure 4), and all

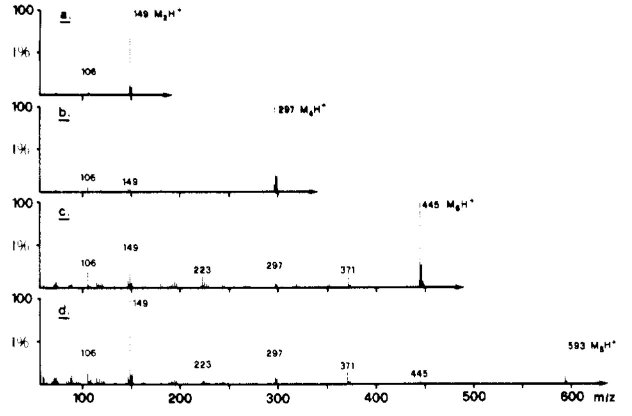

Figure 6. Ammonia chemical ionization mass spectra corresponding to the four cyclic oligomers of polymer II: (a) dimer; (b) tetramer; (c) hexamer; (d) octamer.

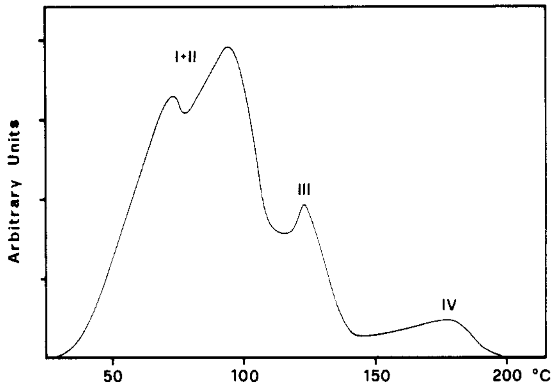

Figure 7. MS total ion current (TIC) vs. temperature of the crude sample of polymer IV: peak I, trimer; peak II, tetramer; peak III, pentamer; peak IV, hexamer.

seven oligomers separated by GPC (Figure 5A) can be safely assigned to cyclic oligomers on the basis of the linear dependence of elution volume on log *M* (Figure 3). Finally, only cyclic oligomers with an even number of repeating units have been detected.

Cyclic Oligomers Formed in the Synthesis of Polymer III. The GPC and MS analysis of the soluble material extracted from the crude sample of polymer III reveals only the cyclic dimer (dithiane).

Cyclic Oligomers Formed in the Synthesis of Polymer IV. Solubility problems do not allow the analysis of the crude polymer IV by GPC to check for oligomer content.

Figure 7 reports the TIC vs. temperature curve for a crude sample of polymer IV, and Figure 8 shows the ammonia CI mass spectra corresponding to the four oligomers detected. Chemical ionization was also preferred in this case because of the low stability of higher oligomers to EI. The ammonia CI spectra of the cyclic sulfides show peaks corresponding to the their molecular ions at m/z 138 and m/z 185, 231, and 277, respectively. In these CI spectra the peak intensities of the M^+ molecular ions are very intense but decrease as the molecular weight of the cyclic sulfides increase (Figure 8).

Conclusions

The foregoing data show the ability of the MS technique to separate and detect the oligomers contained in crude polymeric samples (Figures 1B, 5B, and 7 and Table I). GPC should always be used in the case of soluble compounds, since it affords higher oligomer separation[12] (Figures 1A and 5A and Table I), and therefore the advent of thermospray LC–MS techniques[13,14] may provide a remarkable advance in the field. MS remains, however, an alternative technique in the case of intractable samples (e.g., polymer IV).

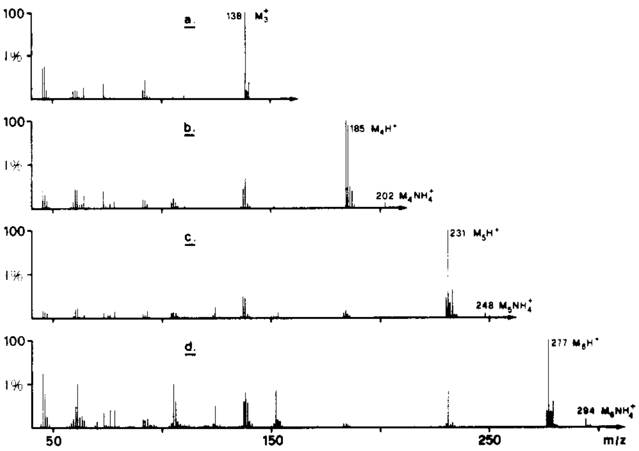

Figure 8. Ammonia chemical ionization mass spectra corresponding to the cyclic oligomers of polymer IV: (a) trimer; (b) tetramer; (c) pentamer; (d) hexamer.

In the polycondensation reactions of dibromoalkanes and dithiols leading to polymers I and II, cyclic oligomers containing an even number of repeating units (dimer, tetramer, hexamer,...) have been detected (Table I). For polymer III, only cyclic dimer was observed.

The knowledge of the distribution of the cyclic oligomers produced in the polycondensation reaction leading to polysulfides provides an answer to the question of whether these oligomers are formed from the reacting monomers or by degradation of the polymer. This question is seldom resolved.[3] In the present case, the fact that only an even number of repeating units are contained in the cyclic oligomers formed in the condensation reactions of dibromoalkanes and dithiols (Table I) provides evidence that these oligomers are formed directly from the monomers and not by degradation of the corresponding polymers. However, in the case of polymer IV, the structure of the dihalide (CH_2Cl_2) does not allow conclusions to be drawn.

Acknowledgment. This work was carried out with partial financial support from the Italian Ministry of Public Education and Consiglio Nazionale delle Ricerche, Italy.

Registry No. I (SRU), 57514-74-6; I (copolymer), 71693-88-4; II (SRU), 28758-48-7; II (copolymer), 104035-44-1; III (SRU), 24936-67-2; III (copolymer), 104035-45-2; IV (SRU), 24938-55-4; IV (copolymer), 79729-03-6.

References and Notes

(1) Zahn, H.; Gleitsman, G. B. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 410.
(2) Semlyen, J. A. *Adv. Polym. Sci.* **1976**, *21*, 41.
(3) Goethals, E. J. *Adv. Polym. Sci.* **1977**, *23*, 103.
(4) Foti, S.; Montaudo, G. In *Analysis of Polymer Systems*; Bark, L. S., Allen, N. S., Eds.; Applied Science: London, 1982; p 103 and references therein.
(5) Ballistreri, A.; Garozzo, D.; Montaudo, G. *Macromolecules* **1984**, *17*, 1312.
(6) Montaudo, G.; Puglisi, C.; Scamporrino, E.; Vitalini, D. *Macromolecules* **1986**, *19*, 870.
(7) Russo, M.; Mortillaro, L.; De Cecchi, C.; Valle, G.; Mammi, M. *J. Polym. Sci., Polym. Lett. Ed.* **1965**, *3*, 455, 501.
(8) Ochrymowycz, L. A.; Mak, C. P.; Michma, J. D. *J. Org. Chem.* **1974**, *39*, 2079.
(9) Meadow, J. R.; Reid, E. E. *J. Am. Chem. Soc.* **1934**, *56*, 2127.
(10) Rosen, W.; Bush, D. H. *Inorg. Chem.* **1970**, *9*, 262.
(11) Marvel, C. S.; Kotch, A. *J. Am. Chem. Soc.* **1951**, *73*, 481.
(12) Manolova, N. E.; Gitsov, I.; Velichkova, R. S.; Raskov, I. B. *Polym. Bull.* (*Berlin*) **1985**, *13*, 285.
(13) Vestal, M. L. *Science* (*Washington, D.C.*) **1984**, *226*, 275.
(14) Blakley, C. R.; Vestal, M. L. *Anal. Chem.* **1983**, *55*, 750.