Preparation of Block Copolymers with Polymeric Azocarbamate as an Initiator

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Synopsis

Block copolymers containing polystyrene and poly(ethylene oxide) or poly(propylene oxide) segments were prepared via chemical reactions. A stepwise procedure was first employed to prepare macroazocarbamates by capping poly(ethylene oxide) glycols or poly(propylene oxide) glycols and an aliphatic diisocyanate and subsequently by reacting this intermediate with an azobisalcohol. This macroazocarbamate was later used to initiate free radical polymerization at elevated temperatures. Styrene contents, molecular weights, and elastic modulus-temperature relationships were determined.

INTRODUCTION

There have been various attempts to prepare block copolymers via chemical reactions using certain intermediate prepolymers and other monomeric compounds. The aim has been to synthesize prepolymeric azocarbamates that could be used as initiators for the free radical polymerization of a vinyl monomer at elevated temperatures.

In recent years, Baysal et al.[1-4] described the synthesis and characterization of some new polymeric peroxycarbamates that subsequently were used for block copolymerization of ethylene oxide and propylene oxide with vinyl monomers.

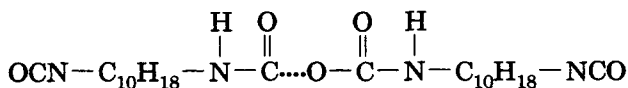Preparation of block copolymers using macroazonitriles has also been described.[5]

In this work, copolymers of styrene-ethylene oxide and styrene-propylene oxide were prepared. This method is based on the following sequence of reactions.
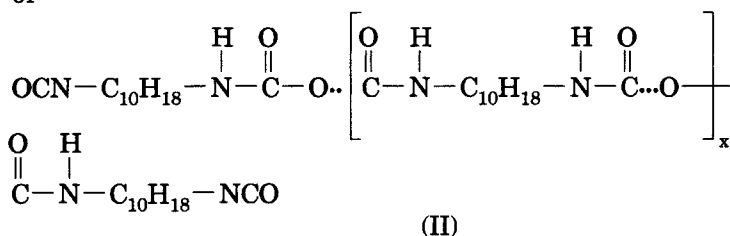
Step 1:

$$\text{HO} \cdots \text{OH} + \text{or } \text{OCN} - \text{C}_{10}\text{H}_{18} - \text{NCO} \longrightarrow$$
1.1
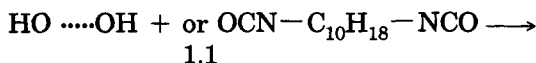
Poly(ether oxide) glycol
Prepolymer   Diisocyanate

$$\text{OCN} - \text{C}_{10}\text{H}_{18} - \overset{\overset{\displaystyle H}{|}}{N} - \overset{\overset{\displaystyle O}{\parallel}}{C} \cdots \text{O} - \overset{\overset{\displaystyle O}{\parallel}}{C} - \overset{\overset{\displaystyle H}{|}}{N} - \text{C}_{10}\text{H}_{18} - \text{NCO}$$

(I)

or

$$OCN-C_{10}H_{18}-\overset{H}{\underset{|}{N}}-\overset{O}{\underset{||}{C}}-O\cdots \left[\overset{O}{\underset{||}{C}}-\overset{H}{\underset{|}{N}}-C_{10}H_{18}-\overset{H}{\underset{|}{N}}-\overset{O}{\underset{||}{C}}\cdots O \right]_{x}$$

$$\overset{O}{\underset{||}{C}}-\overset{H}{\underset{|}{N}}-C_{10}H_{18}-NCO$$
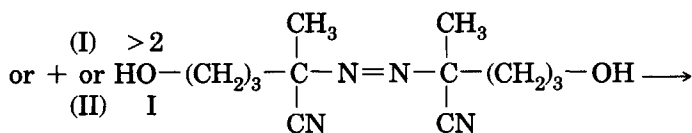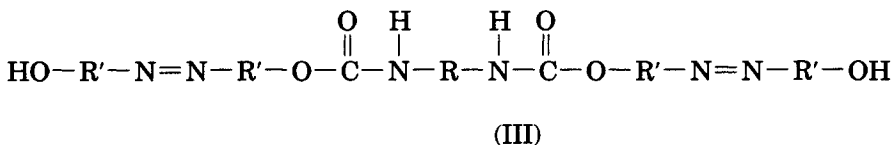
(II)

Compound (I) is the main product when more than 2 mol of the diisocyanate are used[2] in step 1. Compound (I) is an isocyanate-capped prepolymer with hardly any chain extension. Compound (II) results when 1.1 mol of the diisocyanate is used in step 1. Compound (II) is an isocyanate-capped polymer with some chain extension.
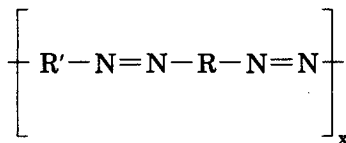
 Step 2:

$$\begin{array}{c}(I) \quad >2 \\ or + or \\ (II) \quad I\end{array} \quad HO-(CH_2)_3-\overset{CH_3}{\underset{CN}{\overset{|}{\underset{|}{C}}}}-N=N-\overset{CH_3}{\underset{CN}{\overset{|}{\underset{|}{C}}}}-(CH_2)_3-OH \longrightarrow$$

Azobiscyanopentanol

$$HO-R'-N=N-R'-O-\overset{O}{\underset{||}{C}}-\overset{H}{\underset{|}{N}}-R-\overset{H}{\underset{|}{N}}-\overset{O}{\underset{||}{C}}-O-R'-N=N-R'-OH$$

(III)

or

$$\left[R'-N=N-R-N=N \right]_{x}$$

(IV)

Here R represents the diisocyanate and prepolymer residues of the chain combined through urethane linkages; and R' shows the residue of azobiscyanopentanol. Compound (III) is the main product when more than 2 mol of the azobiscyanopentanol are used in step 2. Compound (III) is an azocarbamate that can be used as an initiator for the free radical polymerization of a vinyl monomer. Compound (IV) results when 1 mol of the dialcohol is used in step 2. Compound (IV) is a polymeric azo initiator for vinyl polymerization.

 Formation of compounds (III) and (IV) can be accelerated by adding a catalyst, such as dibutyltin dilaurate, to the reaction mixture in step 2.

 Step 3: In this step, Compound (III) or Compound (IV) is used to initiate the free radical polymerization of styrene at elevated temperatures.

 Using the above sequence of reactions, several macroazocarbamates were

prepared as polymerization initiators. The azocarbamate represented by Compound (III) is used to obtain block copolymers of styrene and ethylene oxide.

Characterization of the products were carried out.

EXPERIMENTAL

Materials

Poly(ethylene oxide) glycol (PEG-4000) was a product of Fluka A. G. The molecular weight of PEG-4000 was 4450 (from vapor pressure osmometry). It was dried at 70°C for 3 h under reduced pressure before use.

Poly(propylene oxide) glycol (PPG-2025) was supplied by Fluka A. G. The molecular weight of PPG-2025 was 2025. It was dried at 70°C for 3 h under reduced pressure before use.

3-Isocyanatomethyl-3,5,5-trimethyl-cyclohexyl-isocyanate (IPDI) was a product of Chemische Werke Hüls A.G. It was distilled under reduced pressure before use. Its purity, determined by isocyanate analysis, was better than 99%.[6]

Hydrazine sulfate was a producet of Merck A.G.

Acetopropanol was a product of Aldrich Co. and was used without purification.

Sodium cyanide was a product of Merck A.G.

Styrene was a product of Fluka A.G. It was washed with 5% NaOH solution and H_2O, dried with $CaCl_2$, and freshly distilled under reduced pressure before use.

Dibutyltin dilaurate (T-12) was a product of Cincinnati Milacron Chemicals Inc. and was used without any purification.

Chloroform, toluene, benzene, dichloromethane, and petroleum ether were products of Merck A.G. These were used after drying with $4\times$ molecular sieves.

Methanol was supplied by Kromeklo Laboratories and used after purification.

Procedure

Preparation of γ, γ'-Azobis-(γ-cyano-n-pentanol) (AXO-BCP)

This azo compound was prepared by slow addition of sodium cyanide into the water solution of acetopropanol and hydrazine sulfate according to the method of Bamford et al.[7] The isomer, which is soluble in chloroform, is used in this work (M.P., 99–102°C).

Preparation of Macroazocarbamates (MAC)

The prepolymer, PEG-4000, and the isophorone diisocyanate (IPDI) were reacted at 80°C in toluene solution under a blanket of dry nitrogen. The molar ratio of the diisocyanate to the prepolymer was either more than 2 or 1.1, and the reaction period was over 40 h. The resulting product was

dissolved in dichloromethane, precipitated in a large excess of petroleum ether, and dried in vacuo at 25°C for 24 h. The molecular weight of the product was determined by end-group isocyanate analysis. This product was later dissolved in dichloromethane and a calculated amount of the azobis-alcohol (AZO-BCP) was added together with a few drops of T-12. The mixture was reacted under dry nitrogen at room temperature in the dark for over 48 h. The resulting azocarbamates were isolated by precipitating in petroleum ether and drying in vacuo at room temperature. The molecular weights of the macroazocarbomates were determined by viscometry using the relationship for poly(ethylene oxide)

$$[\eta] = 48 \times 10^{-5} \, \mathbf{M}_n^{0.68} \tag{1}$$

for benzene solutions at 20°C.[8] For poly(propylene oxide),

$$[\eta] = 11.1 \times 10^{-5} \, \mathbf{M}_n^{0.74} \tag{2}$$

for benzene solution at 20°C.[8] These macroazocarbamates were soluble in methanol.

Initial conditions employed for the preparation of six macroazocarbamates and their molecular weights are given in Table I.

Preparation and Characterization of Copolymers

Weighed amounts of the macroazocarbamates were dissolved in predetermined amounts of styrene. The samples were degassed at least four times, sealed, and placed in a constant-temperature bath; polymerization was carried out for desired periods of time. The products obtained were then dissolved in dichloromethane. The copolymer was precipitated in a large excess of methanol. Unreacted initiator and monomer were removed. Polymer was filtered, washed several times with methanol, dried in a vacuum oven at 50°C overnight, and weighed.

TABLE I
Preparation of Macro-Azocarbamates (MAC)

MAC no.	IPDI / PEG-4000	-OH / -NCO	Solubility[a]	$[\eta]$ (dL/g)[b]	$\mathbf{M}_n \times 10^{-3}$
A-1	>2	>2	(x) THF, DMSO DMF	Gel	—
A-2	>2	>2	(o) THF,CH$_2$Cl$_2$, DMF, B, T	0.301	13
A-3	1.1	>2	& &	0.766	51
A-4	1.1	1.0	& &	0.904	66
A-5	>4	>2	& &	0.590	35
A-6	>2[c]	>2	& &	0.104	5.8

[a] (x), Insoluble; (o), soluble.
[b] Benzene, 20°C.
[c] Prepolymer is PPG-2025.

Styrene content of the copolymers was determined by ultraviolet (UV) spectroscopy at 269 nm.[9] This method is based on measuring the absorbance of pure polystyrene, azocarbamate, and copolymer at 269 nm. From the values of the absorbances, the weight percentage of styrene in the copolymer can be calculated by using the equation

$$\% \text{ Styrene} = \frac{\epsilon_c - \epsilon_{ac}}{\epsilon_{ps} - \epsilon_{ac}} \times 100 \tag{3}$$

where ϵ_c, ϵ_{ac}, and ϵ_{ps} are specific extinction coefficients of the copolymer, azocarbamate, and polystyrene, respectively. Molecular weights of the copolymers were determined using the equation

$$[\eta] = 44 \times 10^{-5} \, \mathbf{M}_n^{0.65} \tag{4}$$

given for toluene solutions at 25°C.[10]

The infrared spectra were determined using a Perkin-Elmer 177 Spectrometer with a 1-mm NaCl cell. Dichloromethane was used as a solvent.

The elastic modulus (10 s) was measured using a Gehman-Torsion Stiffness Tester of the American Instrument Co. The calibration of the torsion wires used in measurements and calibration of Young's modulus is based on ASTM D-1053-58T. For mechanical tests, copolymeric samples were compression molded at 135–140°C.

Initiation of Styrene Polymerization by Macro-azocarbamates

Calculated amounts of macroazocarbamate (MAC-No. 2, Table I) and styrene monomer were introduced into pyrex reaction tubes and evacuated on the high vacuum system. Then the tubes were sealed and put into a constant-temperature bath at 80°C. Conversions were kept below 10% by weight for reliable kinetic analysis of the data obtained. Rate R_p and average degree of polymerization $\mathbf{P}_n$ were calculated from the conversion-time data and dilute solution viscosity measurements, respectively. Equation (4) was used for molecular weight calculations.

RESULTS AND CONCLUSIONS

Using one of the macroazocarbamate samples (MAC-No. 2) described in Table I, seven copolymers of styrene and poly(ethylene oxide) were synthesized. Table II contains the initial conditions and other related data for these copolymers. All bulk copolymerization runs were carried out under vacuum. The weight percentage of soft material incorporated into the polymeric product ranged from 8.7 to 24.4%.

The polymerization temperature was not programmed.[3] However, polymerization was started at 80°C and ended at 100°C in order to obtain a size distribution of the vinyl blocks with no unreacted azo groups left imbedded in the copolymer. Overall conversions were rather high as seen in Table II.

TABLE II
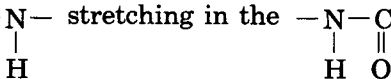Preparation of Styrene and PEG Copolymers in Bulk

Copolymer no.	Macroazocarbamate (wt%)[a]		Polymerization		Conversion (wt%)	$[\mu]$ (dL/g)	$M_n \times 10^3$
	Initial	Found[b]	Time (h)	Temperature (°C)[c]			
1	11.8	8.7	70	80–100	71.7	1.004	147
2	14.3	11.1	70	80–100	92.1	0.881	120
3	15.3	—	70	80–100	77.9	0.817	107
4	18.2	17.1	70	80–100	89.7	0.927	130
5	23.7	19.5	70	80–100	87.3	0.823	108
6	25.2	23.4	70	80–100	89.0	0.790	101
7	30.4	24.4	70	80–100	82.2	0.708	86

[a] Macroazocarbamate (MAC-No. 2) given in Table I.
[b] These values were obtained by subtracting the weight percentage of styrene from 100.
[c] Polymerization was started at 80°C and was elevated to 100°C for the last 5 h.

The course of diisocyanate and γ, γ'-azobis(γ-cyano-n-pentanol) capping reactions was observed by their infrared spectra. In the infrared spectra of copolymers (Fig. 1) peaks at 3340 cm^{-1} were observed in all runs. This absorption is due to the $-\underset{\underset{\text{H}}{|}}{\text{N}}-$ stretching in the $-\underset{\underset{\text{H}}{|}}{\text{N}}-\underset{\overset{\|}{\text{O}}}{\text{C}}-$ group of the azocarbamate. The presence of this absorption peak in the spectrum indicates the incorporation of carbamate in the copolymer chain, which constitutes proof for block polymer formation.

In Fig. 2, elastic modulus-temperature relationships of some of the copolymers prepared in bulk are reproduced. This figure also contains the same relationship for a polystyrene sample. Random copolymers have sharp transition temperatures; block and graft copolymers exhibit a slow decrease in the elastic modulus over a wide range of temperature.[11,12] It should be mentioned that although copolymers 1, 6, and 7 contained varying amounts of soft material, the transition temperatures for these polymers, as estimated from the curves in Fig. 1, were only a few degrees lower compare to polystyrene.

Low-temperature transition of soft component (PEO or PPO) was not observed. The copolymers were not transparent but show a white, milky appearance. However, an obvious phase separation was not observed.

Kinetics of Low-Conversion Styrene Polymerization

The macroazocarbamate (MAC-No. 2) was utilized as a free radical initiator for the polymerization of styrene at 80°C, in bulk. Conversions were kept below 20% for analysis of kinetic experiments. The rate R_p and degree P_n of polymerization were determined from conversion data and viscometric measurements, respectively. The results are given in Table III.

Rate of initiation R_i and rate of polymerization of a free radical polymerization are given by[13-15]
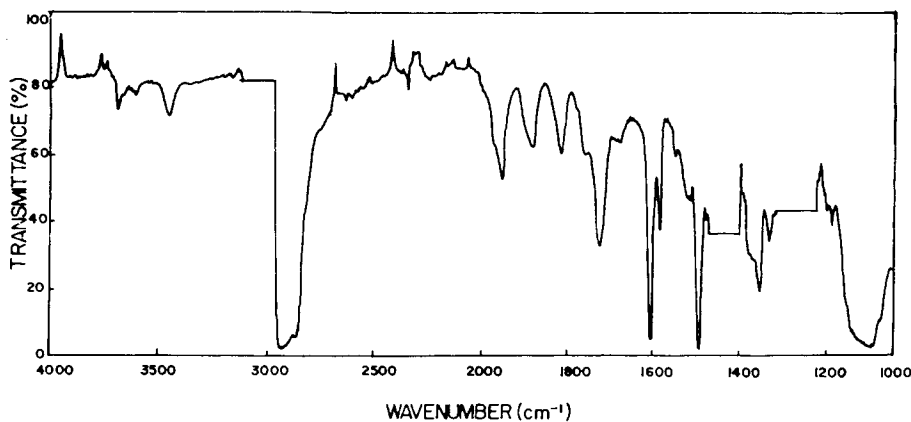
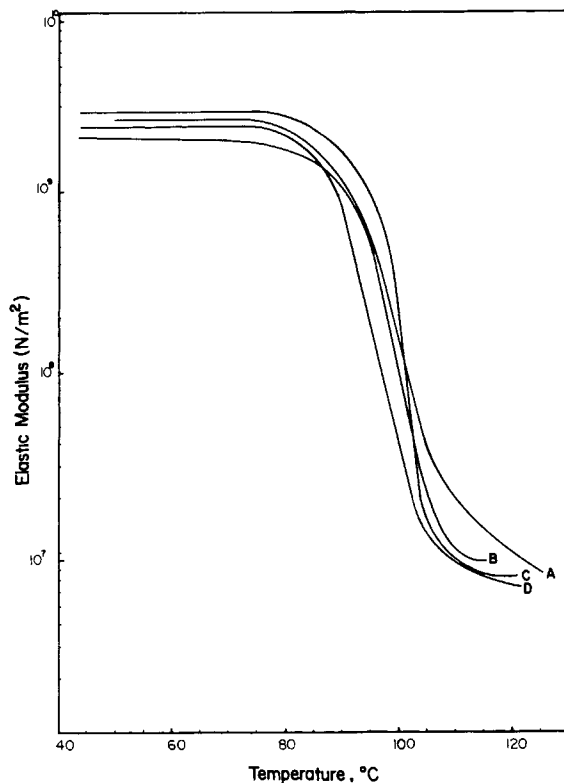$$R_i = 2fk_d[I] \tag{5}$$

Fig. 1. IR spectrum of copolymer.[6]

Fig. 2. Elastic modulus-temperature relationship for various copolymers. Run numbers (listed in Table II): A, 1; B, 6; C, 7; D, PS (MW = 140,000).

and

$$R_p = k_p \left(\frac{fk_d}{k_t}\right)^{\frac{1}{2}} [M] [I]^{\frac{1}{2}} \tag{6}$$

where $[I]$ and $[M]$ are the initiator and monomer concentrations and k_d, k_p, and k_t are the thermal decomposition of the initiator, polymerization, and termination rate constants, respectively; f is called the initiator efficiency. The term $k_p(fk_d/k_t)^{1/2}$ is sometimes denoted as an empirical overall polymerization rate constant K, and its square K^2 is a measure of the initiator reactivity for a particular monomer. The value of K^2 can be obtained from the slope of the plot of R_p^2 versus $[M]^2[I]$, as can easily be seen from eq. (6). For our system it is estimated to be 6.45×10^{-7} L mol^{-1} s^{-2}, from Fig. 3.

For a free radical, bulk polymerization inverse average degree of polymerization $(1/P_n)$ is given as[13-15]

$$\frac{1}{P_n} = C_M + \frac{k_t}{k_p^2 [M]^2} R_p + \frac{C_I}{K^2[M]^3} R_p^2 \tag{7}$$

TABLE III
Polymerization of Styrene with Azocarbamate (at 80°C)

| Run no.	$[I]_o \times 10^4$ (mol/L)	$[M]_o$ (mol/L)	Time (min)	Yield (wt%)	$R_p \times 10^4$ (mol/L·s)	$[\mu]$ (dL/g)	$(1/P_n) \times 10^3$
1	26.9	7.89	80	19.25	3.28	0.402	2.91
2	18.9	7.98	85	16.55	2.65	0.556	1.63
3	16.8	8.00	50	10.33	2.81	0.481	2.20
4	13.6	8.03	90	11.04	1.88	0.628	1.46
5	11.1	8.06	70	10.66	2.07	0.607	1.54
6	10.1	8.07	100	13.61	1.85	0.685	1.28
7	5.81	8.11	120	11.13	1.44	0.746	1.12
8	4.11	8.13	150	9.77	1.02	1.000	0.714
9	4.07	8.13	90	8.48	0.918	0.823	0.963
10	1.26	8.15	120	6.28	0.713	1.304	0.475
11	0.749	8.17	140	6.38	0.620	1.340	0.455
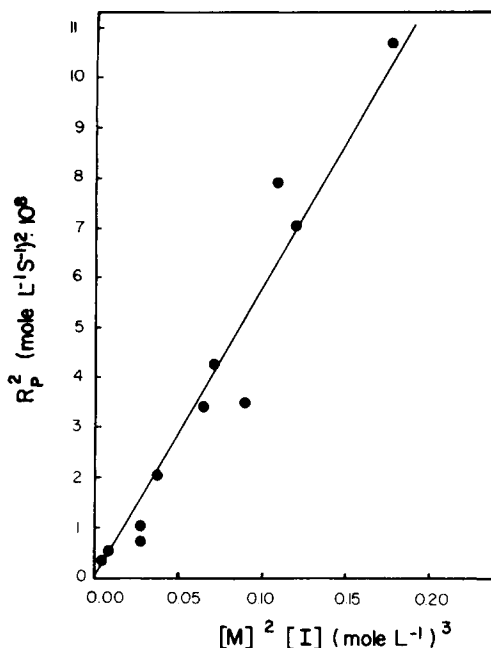
Fig. 3. Plot of R_p^2 versus $[M]^2$ $[I]$ for styrene. Polymerization in bulk at 80°C, initiated by macroazocarbamate.

Here C_M and C_I represent the chain transfer-to-monomer and chain transfer-to-initiator constants, respectively. If $C_I = 0$, a plot of $1/\mathbf{P}_n$ against $R_p/[M]^2$ should yield a straight line (the monoradical line). Such a plot is shown in Fig. 4 for our system. The curvature observed at high $R_p/[M]^2$ values results from the chain transfer to the initiator. The intercept of this curve with $1/\mathbf{P}_n$ axis gives C_M. For our system it is estimated to be 7×10^{-5} and is in good agreement with literature values.[1,13,16]

In order to determine C_I, eq. (7) was rearranged and $1/\mathbf{P}_n - C_M - (k_t R_p/ k_p^2 [M]^2)$ was plotted against $R_p^2/K^2 [M]^3$. This plot is represented in Fig. 5. From the slope C_I is determined as 2.52.

Values of K^2 and $R_i/[I]$ for various initiators are tabulated in Table IV. It should of course be noted that some initiator molecules listed in this table contain more than one decomposing bond or group per molecule. Therefore, $R_i/[I]$ values must be divided by this number for a reliable comparison. Such a comparison indicates that the macroazocarbamates can be used as effective polymerization initiators.

The initiation reaction of structure (III) produces diradicals in the presence of monoradicals. In a free radical polymerization of styrene, termination reactions proceed by combination of radicals. The formation of PS-homopolymer in the presence of diradicals is greatly reduced.[1-4] Nevertheless, an appreciable amount of PS-homopolymer will be present in our copolymeric product. The presence of PS-homopolymer in copolymeric samples could be eliminated by using a polymeric initiator, such as represented
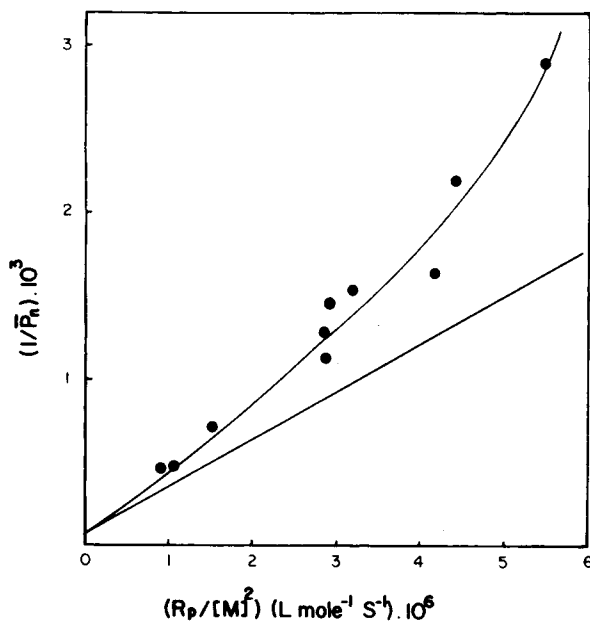
Fig. 4.   Plot of $1/P_n$ versus $R_p/[M]^2$ for styrene polymerization in bulk at 80°C, initiated by macroazocarbamate.
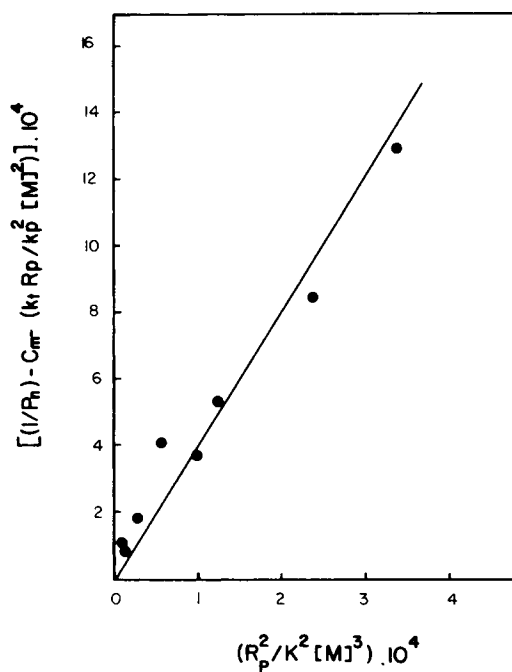

Fig. 5.   Plot of $1/P_n - C_M - k_t R_p/k_p^2$ $[M]^2$ versus R_p^2/K^2 $[M]^3$ for styrene polymerization in bulk at 80°C, initiated by macroazocarbamate

TABLE IV
Polymerization of Styrene at 80°C by Various Free Radical Initiators.

Initiator	$K^2 \times 10^8$ $(\text{l mol}^{-1}\,\text{s}^{-1})^2$	$R_i[I]^{-1}$ (s^{-1})	Number of decomposed bonds per molecul	Reference
Macroazocarbamate	64.5	3.75×10^{-4}	2	This work
Bis (α-cumylperoxycarbamate) polyether	5.29	3.08×10^{-5}	2	1
Polymeric peroxycarbamate (PC-1)	3.29	1.92×10^{-5}	6	17
Luperox-2.5-2.5[a]	0.60	3.52×10^{-6}	2	15
Benzoyl peroxide	11.02	6.42×10^{-5}	1	18
Cumene hydroperoxide	1.28	7.46×10^{-6}	1	18
t-Butylhydroperoxide	0.20	1.64×10^{-6}	1	18
2-Bisazoisobutyronitrile	20.9	1.70×10^{-4}	1	18

[a] 2,5-Dimethyl-2,5-dihydroperoxyhexane.

by structure (IV). Our results on the copolymer formation by using a macroinitiator (IV) will be reported subsequently.

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