

Synthesis of Macroazoinitiator by Direct Polycondensation for Block Copolymerization of Styrene and Butadiene

JOSHY SIMON,¹ ANJALI BAJPAI²

¹ U. D. N. Bajpai's Polymer Research Laboratory, Department of Post-Graduate Studies and Research in Chemistry, Rani Durgavati University, Jabalpur 482 001, India

² Department of Chemistry, Government Model Science College (Autonomous), Jabalpur 482 001, India

Received 31 October 2000; accepted 16 April 2001

ABSTRACT: Macroazoinitiator (MAI) was prepared from hydroxy-terminated polybutadiene (HTPB) and 4,4'-azobis-4-cyanopentanoic acid (ACPA) by direct polycondensation in the presence of 1-methyl-2-chloropyridinium iodide (MCPI) at room temperature. This MAI proved to be an effective initiator for thermal polymerization of styrene at 60°C. The resulting products were characterized by viscosity measurements and both IR and NMR spectral studies. The ratio of styrene and butadiene units was calculated from NMR spectral data and scanning electron micrography. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2922–2933, 2001

Key words: macroazoinitiator; styrene–butadiene block copolymer; hydroxy-terminated polybutadiene; polycondensation; 4,4'-azobis-4-cyanopentanoic acid

INTRODUCTION

Styrene and butadiene block copolymers are of considerable technical importance, and have usually been synthesized by anionic polymerization methods that require rigorous reaction conditions. There always has been a search for some alternative economic radical polymerization methods that have a much wider scope. In recent years there has been a growing interest in the use of macroinitiators for block copolymer synthesis.^{1–7}

It was previously reported that polyesters and polyamides are readily prepared from 4,4'-azobis-4-cyanopentanoyl chloride (ACPC) and diols or diamines in high yield and have been effective as macroazoradical initiators for the synthesis of block copolymers.^{8–11} However, the synthetic process has a disadvantage that a relatively low yield (<53%) of the acid chloride intermediate ACPC is

obtained by the reaction of 4,4'-azobis-4-cyanopentanoic acid (ACPA) with thionyl chloride. To improve the overall yield of condensation polymers from ACPA, the direct polycondensation of ACPA with diols or diamines might be preferable to the indirect method via ACPC because it would eliminate the step for isolation of ACPC.

Mukaiyama et al.^{12–14} reported the condensation of carboxylic acids with some alcohols or amines using 1-methyl-2-halopyridinium salts as a condensation reagent under mild reaction conditions.

Matsukawa et al.^{15,16} reported the direct polycondensation of ACPA with some diols or diamines using 1-methyl-2-chloropyridinium iodide (MCPI) as a condensation reagent and the macroazoinitiators (MAI) thus obtained were examined for the polymerization of typical vinyl monomers.

The present communication reports the direct polycondensation of ACPA with hydroxy-terminated polybutadiene (HTPB) using MCPI as condensation reagent at room temperature and sub-

Correspondence to: A. Bajpai.

Journal of Applied Polymer Science, Vol. 82, 2922–2933 (2001)
© 2001 John Wiley & Sons, Inc.

Table I Results of Direct Polycondensation of HTPB with ACPA^a

Run No.	HTPB		ACPA		CH ₂ Cl ₂ , (ml)	Time, (h)	PBACP				
	mmol	g	mmol	g			Yield		Viscosity data		
							g	%	[η]	<i>k'</i>	<i>k''</i>
1	2.5	5.00	2.5	0.7007	90	18	4.85	85.1	0.370	0.3883	0.1264
2	2.5	5.00	2.5	0.7007	36	18	5.36	94.0	0.580	0.4300	0.1161
3	2.5	5.00	2.5	0.7007	60	8	4.77	83.7	0.361	0.3300	0.1611
4	2.5	5.00	2.5	0.7007	60	18	5.04	88.4	0.380	0.3475	0.1509
5 ^b	—	—	—	—	—	—	—	—	0.138	0.1571	0.1481

^a MCPI, 5.25 mmol; Et₃N, 10.50 mmol; temperature, 27°C.

^b The viscosity measurements of HTPB alone were carried out.

sequent block copolymerization of styrene using this macroazoinitiator.

EXPERIMENTAL

Materials

Hydroxy-terminated polybutadiene (HTPB, a gift from Vikram Sarabhai Space Centre, Thiruvananthapuram, India) was purified by repeatedly washing with methanol, after which it was vacuum dried. The monomers styrene (John Baker Inc., Colorado), and acrylonitrile (Thomas Baker, London, UK) were vacuum distilled prior to use. ACPA and MCPI of AR grade, obtained from Fluka Chemie, (Buchs, Switzerland) and Merck (Darmstadt, Germany), respectively, were used as received. Triethylamine (Bharat Dye-Chem Industries, Bombay, India) and benzene (E. Merck

India Ltd., Bombay, India) of AR grade were used as received. The other solvents dichloromethane, diethyl ether, and methanol (all from Qualigens, India of AR grade) were used without further purification.

Synthesis of Block Copolymers

Polycondensation of ACPA and HTPB

A dichloromethane solution of 2.5 mmol of ACPA and 5.25 mmol of MCPI was stirred for 5 min at room temperature. Triethylamine (5.25 mmol) was added to this suspension at 5°C and maintained at room temperature for 30 min. Successively, 2.5 mmol of HTPB and then 5.25 mmol of triethylamine were added to this mixture. The mixture was stirred for the required time at room temperature. The dark yellow suspension was washed with water by using a separating funnel

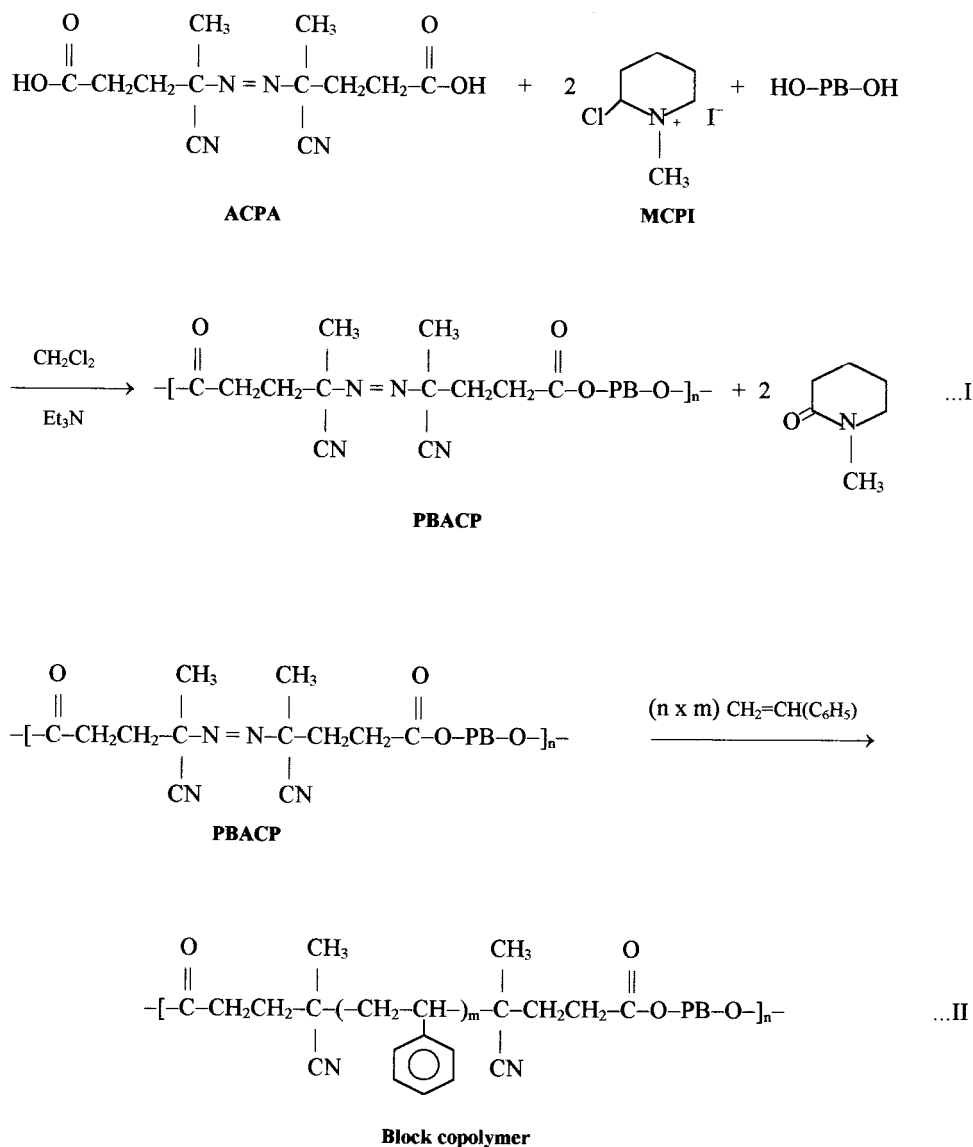
Table II Polymerization of Styrene Initiated with MAI^a

Run No.	PBACP			Styrene		Yield		Conversion (%)	[η] (dL/g)	Increase in [η] ^b (%)	<i>k'</i>	<i>k''</i>
	—(—N=N—) ^c (mmol/L)	g	[η]	mol/L	g	g	%					
1	13.90	0.6233	0.370	0.721	1.50	1.1166	52.6	32.9	0.508	37.3	0.3548	0.1500
2	13.90	0.6233	0.370	0.963	2.00	1.6300	62.1	50.3	0.618	67.0	0.3669	0.1417
3	13.90	0.6233	0.370	0.480	1.00	0.7350	45.3	11.2	0.465	25.7	0.3570	0.1480
4	7.54	0.3381	0.370	0.721	1.50	0.7025	38.2	24.3	0.537	45.1	0.3548	0.1495
5	3.77	0.1691	0.370	0.721	1.50	0.4100	24.6	16.1	0.575	55.4	0.3670	0.1396
6	13.90	0.6233	0.380	0.963	2.00	1.1100	42.3	24.3	0.681	79.2	0.3670	0.1419
7	13.90	0.6233	0.380	0.963	2.00	1.1300	43.1	25.3	0.481	26.6	0.3573	0.1478

^a Reaction temperature, 60°C; reaction time, 24 h; solvent for runs 1–5: benzene; solvent for run 6: *n*-hexane; and solvent for run 7: chloroform.

^b Percentage increase in intrinsic viscosity of PBACP on copolymerization with styrene.

^c Calculated from presumed formula weight per an azo unit.



Scheme 1 Formation of block copolymer of styrene and butadiene. I: Polycondensation of ACPA and HTPB in the presence of MCPI to obtain the macroazoinitiator PBACP; II: Radical polymerization of styrene in the presence of PBACP to produce styrene-butadiene block copolymer.

and the dichloromethane layer was separated and dried with calcium chloride and evaporated under reduced pressure. A highly viscous liquid was obtained. This was washed with a minimal amount of diethyl ether. It was further purified by completely dissolving in excess diethyl ether and reprecipitating by addition of methanol. The polyester poly(polybutadiene-4,4'-azobis-4-cyanopentanoate) (PBACP) obtained was then dried in vacuum and weighed. The yield was calculated using the formula

$$\begin{array}{l}
 \text{Yield (\%)} \\
 = \frac{\text{Weight of polyester (PBACP) obtained}}{\text{ACPA in feed} + \text{HTPB in feed}} \\
 \times 100 \quad (1)
 \end{array}$$

Radical Polymerization of Styrene Using PBACP

A benzene solution of given amounts of PBACP and styrene was placed in a Pyrex glass test tube, passed under nitrogen gas for 30 min. The glass tube was then tightly stoppered. The polymeriza-

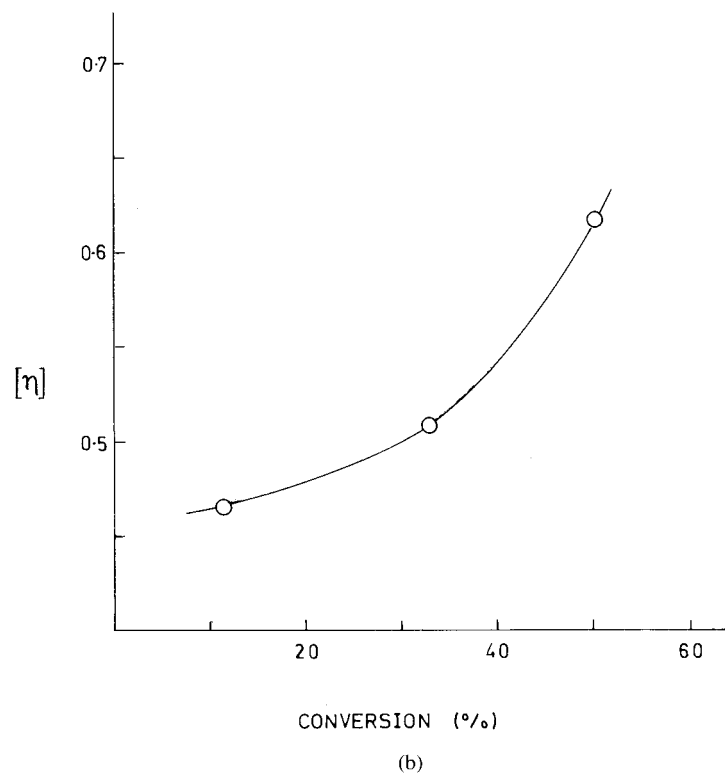
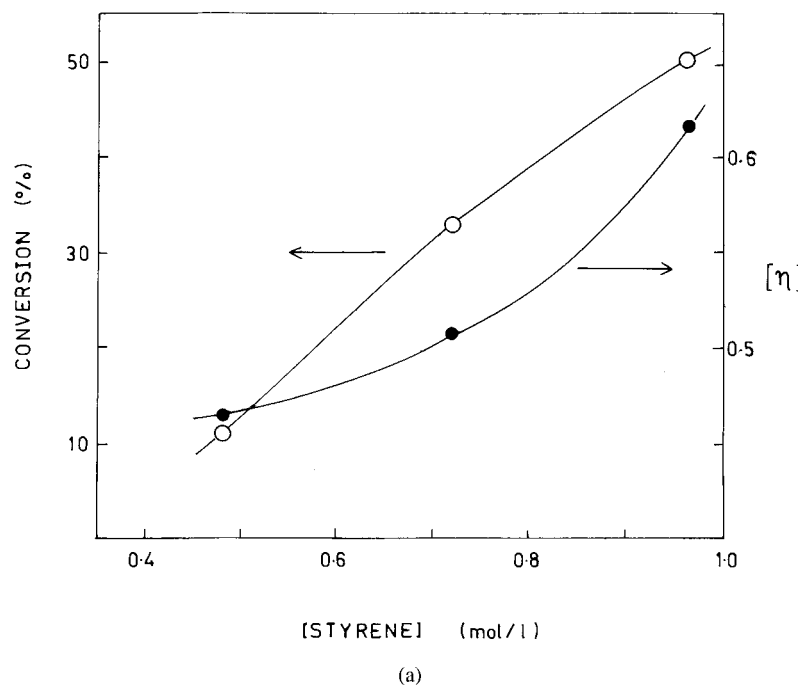


Figure 1 (a) Effect of concentration of styrene on percentage conversion and intrinsic viscosity at constant MAI concentration. (b) Relationship between percentage conversion and intrinsic viscosity at constant MAI concentration.

tion was carried out at 60°C for 24 h, by intermittent shaking of the solution, and kept in a constant temperature bath. The block copolymer was

precipitated by pouring the reaction mixture into a large volume of methanol. The precipitated polymer was filtered and dried under reduced

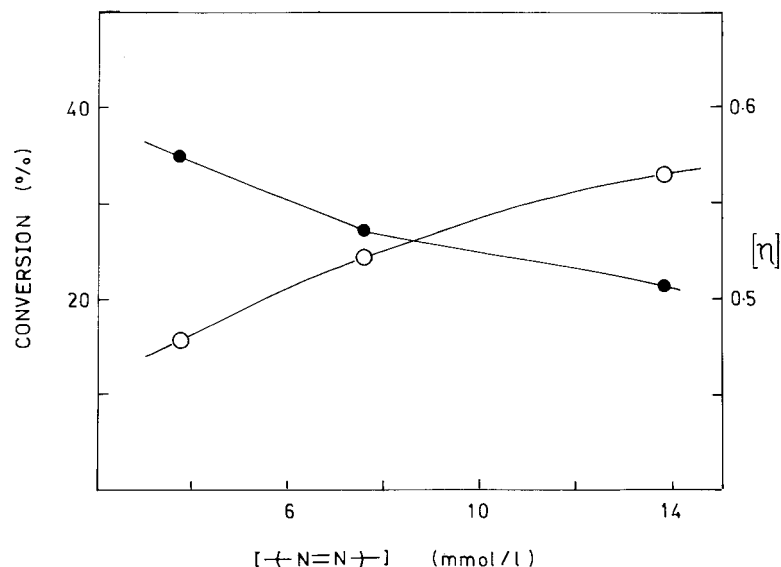


Figure 2 Effect of concentration of MAI on percentage conversion and intrinsic viscosity at constant monomer concentration.

pressure. It was then weighed for the calculation of yield and percentage conversion using eq. 2 and eq. 3, respectively.

$$\text{Yield (\%)} = \frac{\text{Weight of block copolymer}}{\text{PBACP in feed} + \text{monomer in feed}} \times 100 \quad (2)$$

$$\text{Conversion (\%)} = \frac{\text{Yield} - \text{PBACP in feed}}{\text{Monomer in feed}} \times 100 \quad (3)$$

Measurements

The viscosities of dilute solutions of macroazoinitiators (PBACP) and the block copolymers were determined in 0.5–2.0% and 0.25–1.0% (w/v) polymer concentration ranges, respectively, in benzene using a Ubbelohde viscometer. The Huggins' and Kraemer's equations [eqs. (4) and (5)] were used for the calculations.

$$\eta_{sp}/C = [\eta] + k'[\eta]^2C \quad (4)$$

$$\ln \eta_r/C = [\eta] + k''[\eta]^2C \quad (5)$$

where, $[\eta]$, η_{sp} , and η_r are intrinsic, specific, and relative viscosities, respectively; k' and k'' are Huggins' and Kraemer's constants, respectively; and C is the concentration of polymer in grams per 100 mL. The results of both equations were

plotted using the same graph. The point of intersection of both lines at the ordinate was taken as the intrinsic viscosity.

Infrared spectra of HTPB, an authentic sample of polystyrene, macroazoinitiator (PBACP), and block copolymers were recorded on a Perkin-Elmer Model 1430 spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT) using KBr as a dispersant. $^1\text{H-NMR}$ spectrum was recorded on a Bruker DRX-300 FT-NMR spectrometer (Bruker Instruments, Billerica, MA) in CDCl_3 solution using TMS as an internal standard. Differential scanning calorimetry (DSC) was carried out on a Mettler DSC instrument in nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. The morphology of the block copolymer was examined using a Leica-430 scanning electron microscope (SEM; Leica, Deerfield, IL).

RESULTS AND DISCUSSION

Synthesis of PBACP

The direct polycondensation of ACPA with HTPB (HO-PB-OH) was performed using MCPI as the condensation reagent at room temperature. Dichloromethane was used as a solvent and triethylamine was used as an acceptor of hydrochloric acid.

The details of reaction conditions and results of polycondensation are summarized in Table I. For

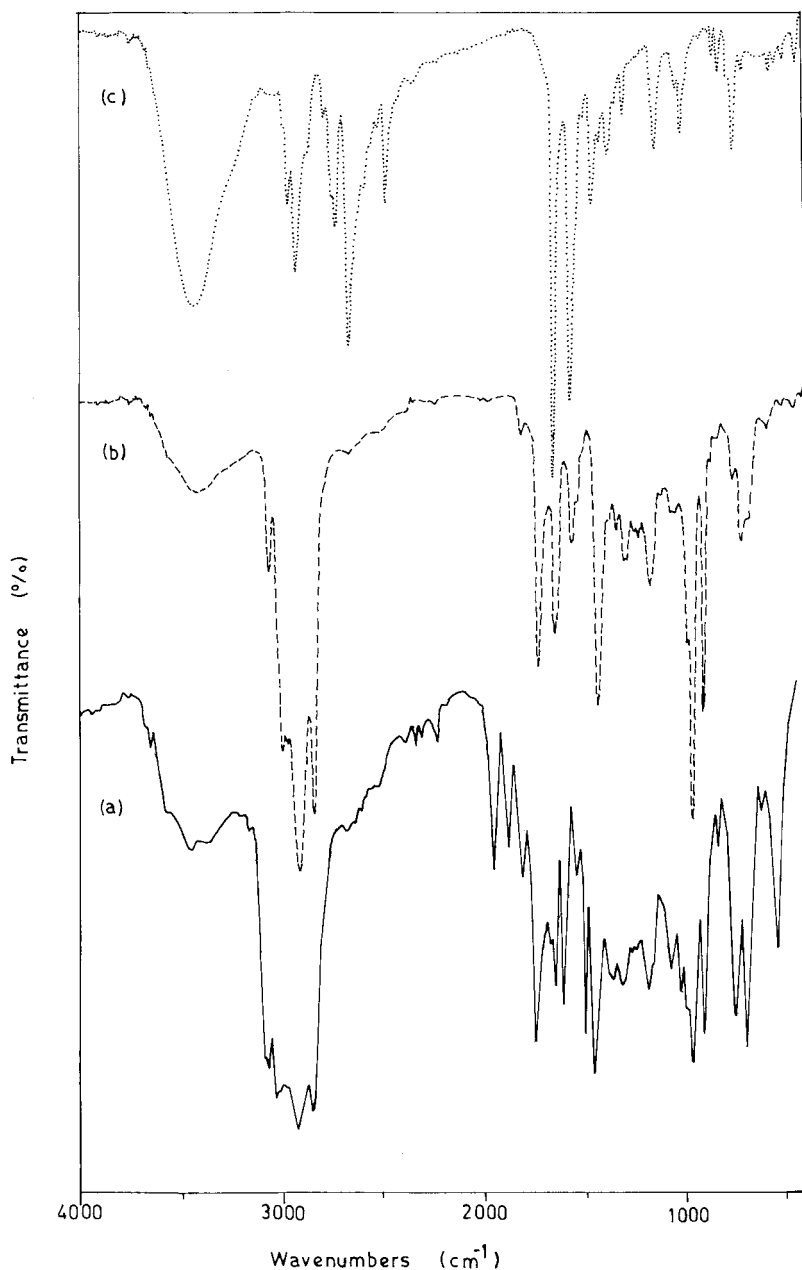


Figure 3 IR spectra of (a) block copolymer, (b) MAI, and (c) ACPA.

all cases the yields were considerably high. The intrinsic viscosities of these macroazoinitiators and HTPB determined by dilute solution viscometry in benzene are also incorporated in Table I. It was observed that the intrinsic viscosity increased almost linearly with the increase in yield of MAI. The intrinsic viscosity is the most common measure of molecular weight for the polymers. A 2.6- to 4.2-fold increase in intrinsic viscosity of PBACP over that of HTPB is a clear indication of incorporation of several polybuta-

diene blocks in MAI on direct polycondensation of HTPB with ACPA.

The condensation of HTPB and ACPA to produce the macroazoinitiator PBACP was confirmed by IR spectroscopy. The IR spectrum of a representative MAI (run 1, Table I) is depicted above in Figure 3.

Polymerization of Styrene with PBACP

The polymerization of styrene was performed by the use of PBACP as the macroazoradical initia-

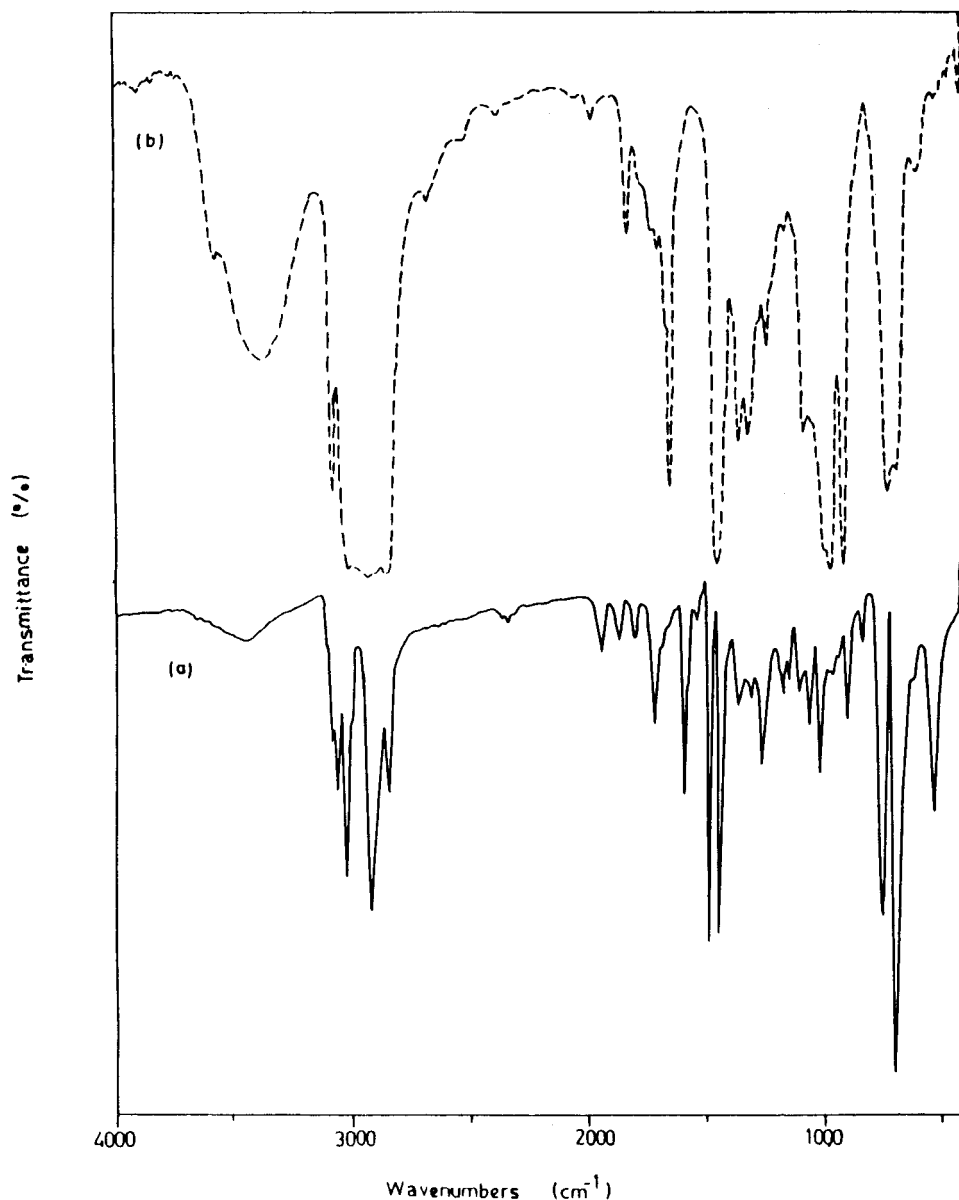


Figure 4 IR spectra of (a) polystyrene and (b) HTPB.

tor in benzene at 60°C for 24 h. The polymerization time was prolonged so that almost all the azo groups could be completely decomposed. The results of polymerization of styrene with this MAI are summarized in Table II.

The products were assumed to be block copolymers because thermal polymerization of styrene monomer did not occur under the same reaction conditions, either in the presence of the prepolymer HTPB or alone. Hence it is very well evident that the block copolymerization took place from radicals formed through the scission of $-N=N-$ units. Similar observations were

also reported by other researchers.^{5,15,17} The block copolymer formation can be presented as in Scheme 1.

Three different solvents were used for the polymerization of styrene in the presence of MAI to find out the solvent effect. However, under the same reaction conditions the change of solvent from benzene to hexane or chloroform lowers the conversion from 50.3 to 24.3 and 25.3%, respectively, indicating that benzene is a better solvent for the polymerization of styrene in the presence of MAI.

The percentage conversion was lesser in hexane than that in chloroform and benzene but the

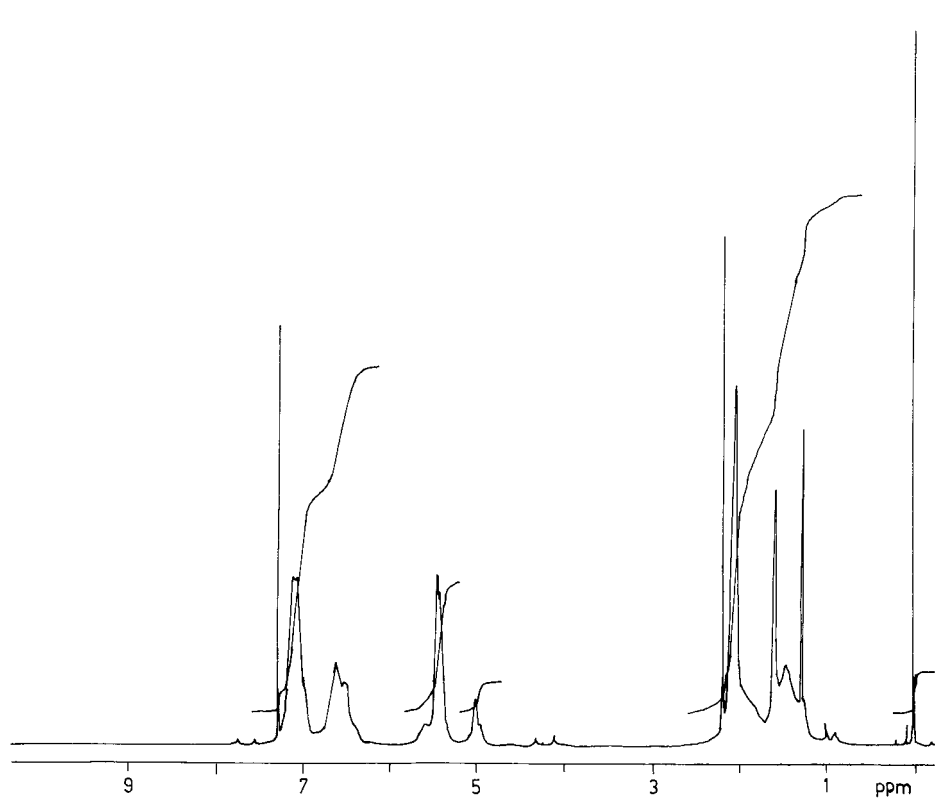


Figure 5 ^1H -NMR spectrum of block copolymer.

percentage increase in viscosity was higher. This is probably an indication of the fact that the mutual reaction of the macroradicals is facilitated in a poor solvent. Thus, instead of a propagation reaction with styrene monomer the macroradicals generated by the scission of azo bonds combine themselves. A similar finding was also reported by Yamada et al.³

In chloroform the yield was lesser than that in benzene and the product on selective extraction indicated the presence of some polystyrene. However, polystyrene could not be detected in the product obtained in benzene solution. The chain transfer constant for styrene is greater for chloroform, hence it is suggested that some homopolystyrene may also form through the chain transfer to chloroform, although the quantitative separation of polystyrene was not possible through selective extraction with solvents.

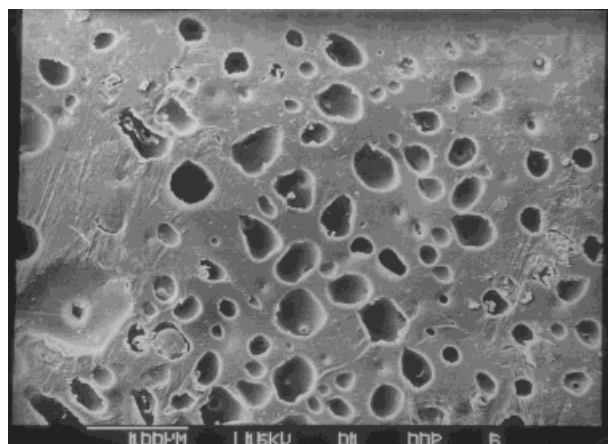
Figure 1(a) shows the effect of concentration of styrene on percentage conversion and on intrinsic viscosities $[\eta]$, at a constant MAI concentration. It is evident from this figure that with the increase in concentration of styrene the percentage conversion as well as intrinsic viscosities increased, in-

dicating incorporation of a greater number of styrene units in the block copolymer.

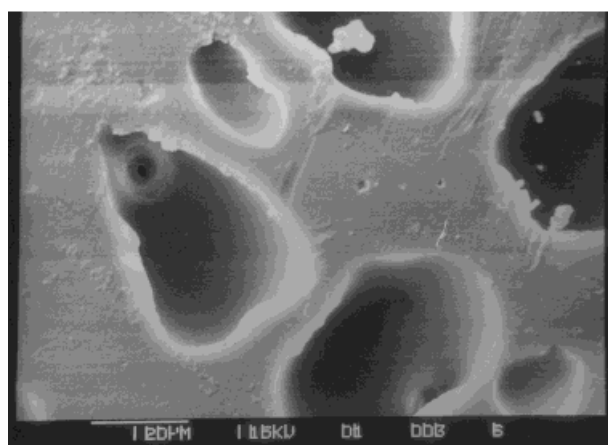
Figure 1(b) shows the relationship between conversion and intrinsic viscosity at a constant MAI concentration and an increase in intrinsic viscosity is indicated with the increase in conversion. This supports the accepted view that a definite difference between the ordinary initiator system and the macroinitiator system exists in the molecular weight of the polymer produced.¹⁸ Ueda and Nagai⁶ concluded that, although polymers obtained in the ordinary initiator system show almost the same average molecular weight independent of the conversion, polymers obtained

Table III NMR Spectral Data of the Styrene-Butadiene Block Copolymer

Proton	Frequency (ppm)	Relative Intensity
Aromatics	7.26220–7.05223	1.83
Vinyls	5.41277–4.96354	1.00
Methylene (BD units)	2.17414–2.03620	2.11



(a)



(b)

Figure 6 SEM micrograph of block copolymer. Magnification (a) $\times 200$ (b) $\times 1000$.

by a macroinitiator show growth of average molecular weight with an increase in conversion. This occurs because every scissile bond in the macroinitiator molecule decomposes step-by-step, thus connecting the multigrown polymer chain.

Figure 2 shows the effect of concentration of MAI on percentage conversion as well as intrinsic viscosities, at a constant styrene concentration. With the increasing MAI concentration the percentage conversion increased, whereas intrinsic viscosity decreased because, with the increase in the number of initiating species, conversion should increase and the molecular weight should decrease in that the concentration of monomer is kept constant. Nagai et al.⁷ also reported that with increasing MAI concentration percentage conversion increased, whereas the molecular weight decreased in their study of block copoly-

merization of polyvinyl acetate using MAI prepared from different kinds of bisphenols.

Characterization

Formation of MAI by direct condensation of HTPB and ACPA and consequent block copolymer formation by interaction of styrene and MAI is quite evident from a comparison of IR spectra of MAI (run 1, Table I) and block copolymer (run 2, Table II) with those of HTPB, polystyrene, and ACPA. The IR spectra of ACPA, MAI, and block copolymer are depicted in Figure 3 and those of polystyrene and HTPB in Figure 4.

The strong and broad absorption at 3380 cm^{-1} of HTPB, attributed to hydrogen-bonded hydroxyl groups and the broad, intense OH stretching absorption of carboxylic groups of ACPA, appear with greatly reduced intensity in MAI as well as in the block copolymers. The appearance of the intense absorption near 1738 cm^{-1} in MAI and block copolymer clearly shows the presence of ester linkage. The broad and strong absorption ascribed to out-of-plane CH bending of HTPB at 966 cm^{-1} appears with considerable reduction in intensity in MAI. The two intense peaks characteristic of the monosubstituted benzene ring of the polystyrene component in the block copolymer appear at 755 and 699 cm^{-1} . The presence of a polystyrene component in the block copolymer is further evidenced by (1) the presence of aromatic C—H stretching in the 3062 and 3025 cm^{-1} region, (2) skeletal vibrations involving $\nu_{\text{C}-\text{C}}$ within

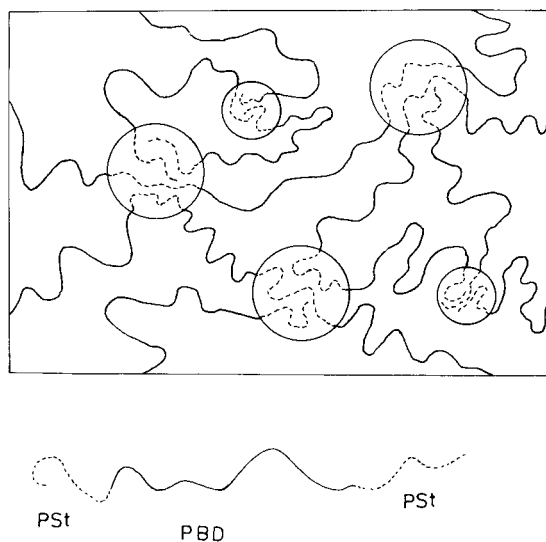


Figure 7 Schematic representation of the block copolymer.

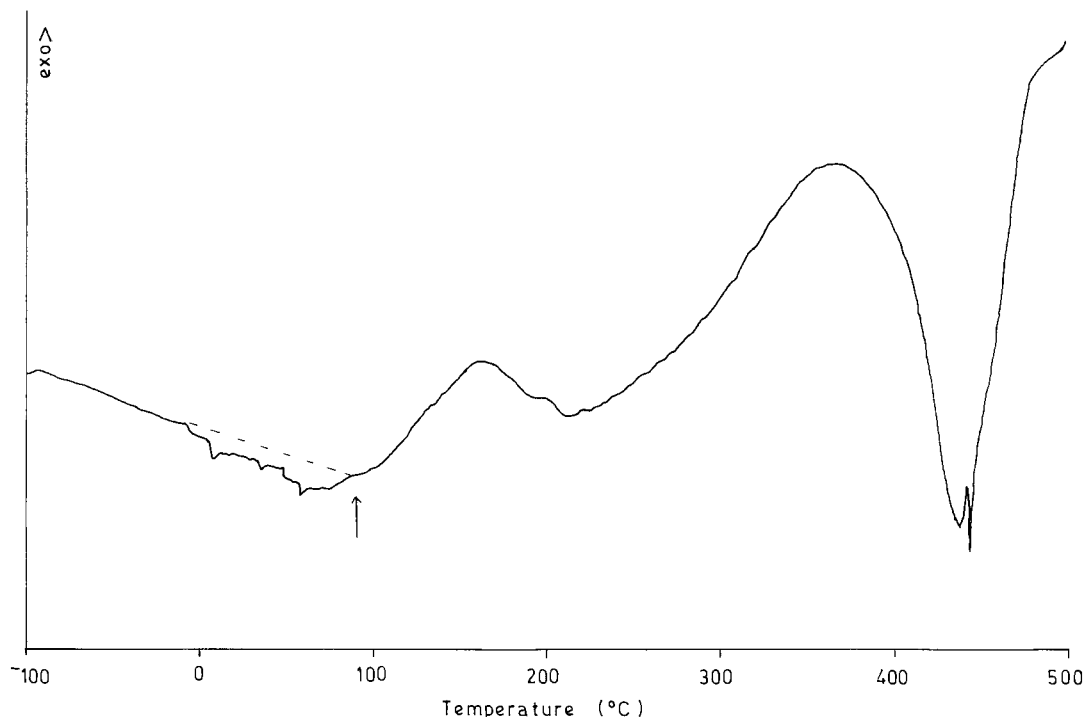


Figure 8 DSC thermogram of block copolymer.

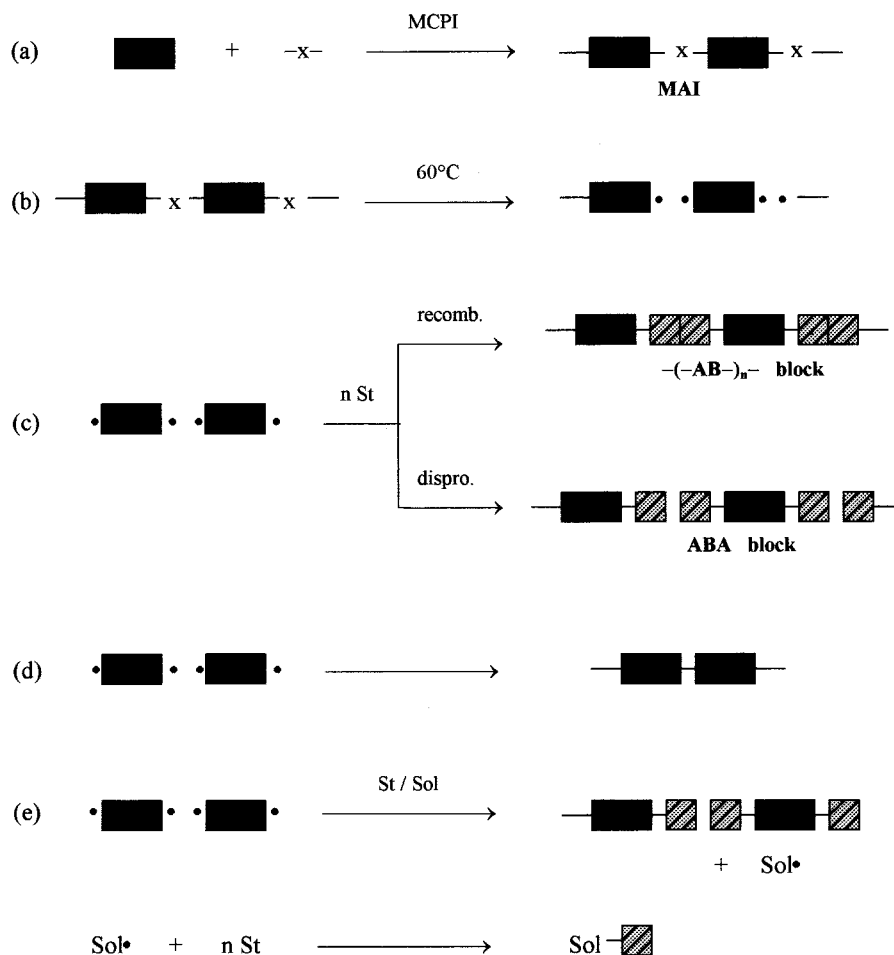
the ring at 1600 cm^{-1} and a doublet in the $1500\text{--}1400\text{ cm}^{-1}$ region, and (3) the characteristic absorption pattern attributed to the monosubstituted benzene ring in the $2000\text{--}1650\text{ cm}^{-1}$ region. The IR spectrum of block copolymers consists of sharp peaks, which is indicative of the purity of the sample, and the semicrystalline nature of the block copolymer can also be inferred.

The $^1\text{H-NMR}$ spectrum of a representative sample (run 2, Table II) of the block copolymer is depicted in Figure 5. The proportion of butadiene and styrene units in the block copolymer was calculated from the NMR data presented in Table III. The sample of HTPB used has a number-average molecular weight of about 2000. From the intensities of the aromatic protons on styrene units and methylene protons on butadiene units, the butadiene-to-styrene ratio in the block copolymer was calculated to be 1.44 : 1 (0.59 : 0.41). The comparison of vinyl protons of butadiene unit and aromatic protons of styrene units gives the butadiene-styrene ratio as 1.38 : 1 (0.58 : 0.42). The close resemblance of the results from these calculations also suggests that the double bonds of butadiene are not affected during the polymerization procedure.

The block copolymers were completely soluble in benzene, chloroform, cyclohexane, toluene, and

the like, hence formation of crosslinked product was ruled out. However, the product exhibited low elongation upon stretching. This may be attributed to the higher styrene content. The reason for this apparent crosslinked behavior probably is that the large polystyrene blocks form glassy aggregates that function as massive crosslinks. This conclusion is supported by the SEM observation of the product (Fig. 6). Microdomains of polystyrene ($10\text{--}40\text{ }\mu\text{m}$) are dispersed in a continuous matrix of polybutadiene. If the surface morphology is considered as the outward manifestation of composition of the block copolymer and the relative areas of different phases as a measure of relative contribution of two components, then the styrene-butadiene proportion is approximately 40 : 60, which is broadly in agreement with that obtained from NMR data.

The schematic representation of the block copolymer is depicted in Figure 7. Circles represent the glassy domains of polystyrene acting as crosslinks holding the polybutadiene segments in place.¹⁹ The independent behavior of the polybutadiene portion is evident from the DSC thermogram (Fig. 8). A very small inflection ascribed to the glass-transition temperature (T_g) of polybutadiene segment is apparent near -50°C . A broad melting endotherm is observed in the -10



Scheme 2 Schematic representation of mechanism of block copolymer formation: (a) polycondensation of prepolymer (HTPB) with ACPA to produce MAI; (b) generation of macroradicals through the scission of the azo group on heating; (c) block copolymerization by reaction of styrene with macroradicals; (d) mutual reaction of macroradicals in poor solvent; and (e) formation of homopolystyrene through chain transfer to solvent. $-\chi-$, scissile bond ($-\text{N}=\text{N}-$); recomb., termination by recombination; \blacksquare , polybutadiene segment (A); dispro., termination by disproportionation; \hatched , polystyrene segment (B); Sol, Solvent.

to 98°C range. The broad range of melting and small area of melting endotherm is indicative of the presence of small crystals in the material. The T_g attributed to the polystyrene segment is obscured by the melting endotherm; however, the inflection at 92.5°C may be considered as the T_g of polystyrene.

Possible Mechanism

On the basis of the results obtained and the preceding discussion the mechanism to generate different classes of inactive polymers is depicted in **Scheme 2**. The macroazoinitiator obtained by direct polycondensation of HTPB with ACPA de-

composes homolytically on heating at 60°C into macroradicals. These macroradicals may initiate the copolymerization of styrene, resulting in the formation of $-(\text{AB})_n-$ or ABA-type block copolymers. Because recombination predominates with polystyryl radicals, a greater proportion of $-(\text{AB})_n-$ is expected. Recombination of the macroradicals as soon as they are formed may predominate in poor solvents like hexane, yielding larger blocks of the butadiene component. Solvents with higher chain transfer constant (e.g., chloroform) may also yield some homopolystyrene. Formation of homopolystyrene through the chain transfer from the growing

block copolymer chain to styrene monomer can be neglected.²⁰

CONCLUSIONS

Macroazoinitiator (MAI) was prepared by direct polycondensation of 4,4'-azobis-4-cyanopentanoic acid (ACPA) with HTPB in the presence of 1-methyl-2-chloropyridinium iodide (MCPI). The MAI was employed for the polymerization of styrene. Formation of block copolymers was confirmed by IR, ¹H-NMR spectroscopy, and viscosity measurements. With the increase in concentration of styrene the percentage conversion as well as intrinsic viscosities increased, reflecting the special feature of the macroinitiator system that every scissile bond in the macroinitiator molecule decomposes step-by-step, thus connecting the multigrown polymer chain. The block copolymers obtained were completely soluble in various organic solvents, suggesting the formation of linear chains. On the basis of low elongation on stretching and the surface morphology observed in SEM it is suggested that the flexible polybutadiene chains are held in position by the glassy domains of polystyrene acting as crosslinks.

REFERENCES

1. Cakmak, I.; Hazer, B.; Yagci, Y. *Eur Polym J* 1991, 27, 101.
2. Ueda, A.; Agari, Y.; Kosai, K.; Nishioka, N.; Nagai, S. *Chem Express* 1992, 7, 725.
3. Yamada, B.; Sataka, M.; Otsu, T. *Chem Express* 1992, 7, 157.
4. Nagai, S.; Terada, H.; Ueda, A. *Chem Express* 1993, 8, 157.
5. Terada, H.; Haneda, Y.; Ueda, A.; Nagai, S. *Macromol Rep* 1994, A31, 173.
6. Ueda, A.; Nagai, S. in *Macroinitiators*; Mishra, M. K., Ed.; *Macromolecular Design: Concept and Practice*; Polymer Frontiers: New York, 1994; Chapter 7, p. 285.
7. Nagai, S.; Takemoto, K.; Ueda, A. *Kagaku to Kogyo (Osaka)* 1996, 70, 92.
8. Ueda, A.; Nagai, S. *J Polym Sci Part A Polym Chem* 1984, 22, 1611.
9. Ueda, A.; Nagai, S. *Kobunshi Ronbunshu* 1986, 43, 97.
10. Ueda, A.; Nagai, S. *J Polym Sci Part A Polym Chem* 1986, 24, 405.
11. Kita, Y.; Ueda, A.; Harada, T.; Tanaka, M.; Nagai, S. *Chem Express* 1986, 1, 543.
12. Mukaiyama, T.; Usui, M.; Shimada, E.; Saigo, K. *Chem Lett* 1975, 1045.
13. Mukaiyama, T.; Toda, H.; Kobayashi, S. *Chem Lett* 1976, 13.
14. Mukaiyama, T.; Aikawa, T.; Kobayashi, S. *Chem Lett* 1976, 57.
15. Matsukawa, K.; Ueda, A.; Inoue, H.; Nagai, S. *Chem Express* 1987, 2, 33.
16. Matsukawa, K.; Ueda, A.; Inoue, H.; Nagai, S. *J Polym Sci Part A Polym Chem* 1990, 28, 2107.
17. Ueda, A.; Nagai, S. *J Polym Sci Part A Polym Chem* 1987, 25, 3495.
18. Ueda, A.; Shiozu, Y.; Hidaka, Y.; Nagai, S. *Kobunshi Ronbunshu* 1976, 33, 131.
19. Rodriguez, F. *Principles of Polymer System*, 2nd ed.; McGraw-Hill: Singapore, 1987; p. 77.
20. Tudos, F. *Acta Chim Tomus* 1965, 44, 403.