

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Copolymers of 3-Methoxy-4-Acryloyloxy-Benzal Phenylimine with Methyl Methacrylate: Synthesis, Characterization and Monomer Reactivity Ratios

R. Balaji<sup>a</sup>; S. Nanjundan<sup>a</sup>

<sup>a</sup> Department of Chemistry College of Engineering, Anna University, Madras, India

**To cite this Article** Balaji, R. and Nanjundan, S.(1998) 'Copolymers of 3-Methoxy-4-Acryloyloxy-Benzal Phenylimine with Methyl Methacrylate: Synthesis, Characterization and Monomer Reactivity Ratios', Journal of Macromolecular Science, Part A, 35: 9, 1527 – 1539

**To link to this Article:** DOI: 10.1080/10601329808007314

**URL:** <http://dx.doi.org/10.1080/10601329808007314>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## **COPOLYMERS OF 3-METHOXY-4-ACRYLOYLOXY-BENZAL PHENYLIMINE WITH METHYL METHACRYLATE: SYNTHESIS, CHARACTERIZATION AND MONOMER REACTIVITY RATIOS**

**R. Balaji**

Department of Chemistry  
College of Engineering  
Anna University  
Madras - 600 025, India

**S. Nanjundan\***

Department of Chemistry  
College of Engineering  
Anna University  
Madras - 600 025, India

**Key Words:** 3 Methoxy-4-acryloyloxybenzal Phenylimine, Methyl Methacrylate,  $^1\text{H-NMR}$ , Copolymerization, Reactivity Ratio

### **ABSTRACT**

Copolymers of 3-methoxy-4-acryloyloxybenzal phenylimine and methyl methacrylate with different feed ratios are synthesized in ethyl methyl ketone using benzoyl peroxide as a free radical initiator at  $70 \pm 1^\circ\text{C}$ . The polymers were characterized by IR and  $^1\text{H-NMR}$  spectroscopic techniques. Copolymer compositions were determined by  $^1\text{H-NMR}$  analysis of the polymers. The monomer reactivity ratios were determined by the application of conventional linearization methods such as Fineman-Rose and Kelen-Tüdös. The molecular weights  $M_n$  and  $M_w$  of the polymers and the polydispersity index were determined by gel permeation chromatography. The intrinsic viscosities and the thermal properties of the homo- and copolymers are also discussed.

## INTRODUCTION

Polymers with reactive functional groups are synthesized, analyzed, and used not only for their macromolecular properties (bulk properties of the polymers) but also for specific end applications [1]. Copolymers formed from amine functional monoethylenic monomers, and acrylic acid are used in electrophoretic coating [2]. Polymers of azomethyne Schiff bases are used as semiconductors [3, 4]. Polyamide imide Schiff's base copolymers are known to exhibit heat resisting properties and used as films and foams [5, 6]. Polymers containing Schiff bases are used as raw materials for drugs, agrochem, and electron devices [7, 8]. Schiff base polymers are used to prepare transition metal complexes [9-11]. Magnetic Iron-Schiff base polymer chelate compounds are used for the preparation of recording magnetic films [12].

The accurate estimation of copolymer composition and determination of reactivity ratios is significant for tailor-making copolymers with required physicochemical properties and in evaluating the end application of copolymers. In the past few decades,  $^1\text{H-NMR}$  spectroscopic analysis has been established as a powerful tool for the determination of tacticity and sequence distribution as well as for the estimation of copolymer composition because of its simplicity, rapidity, and sensitivity [13, 14]. The present article deals with the copolymerization behavior of methyl methacrylate (MMA) with the Schiff base containing monomer, 3-methoxy-4-acryloyloxybenzal phenylimine (MABPI) and the characterization of the copolymers.

## EXPERIMENTAL

Methyl methacrylate (MMA) was freed from the inhibitor by washing with 5% aqueous sodium hydroxide solution followed by distilled water, dried over anhydrous sodium sulphate, and distilled twice under reduced pressure. Benzoyl peroxide (BPO) was recrystallized from a chloroform-methanol (1:1) mixture. All the solvents were distilled before use.

### Synthesis of 3-Methoxy-4-acryloyloxybenzal Phenylimine

Acryloyl chloride was synthesized by reacting acrylic acid (1 mol) with benzoyl chloride (2 mol) [15]. 3-methoxy-4-acryloyloxybenzal phenylimine (MABPI) was synthesized by reacting the Schiff base, 3-methoxy-4-hydroxybenzal phenyl-

imine (0.11 mol) with acryloyl chloride (0.11 mol) at 0 to 5°C in the presence of triethylamine (0.11 mol) in ethyl methyl ketone solution. The quaternary ammonium salt formed was filtered off and the solvent was evaporated to get 3-methoxy-4-acryloyloxybenzal phenylimine.

The formation of the monomer was confirmed by IR and <sup>1</sup>H-NMR techniques. IR (cm<sup>-1</sup>): 3080, 3050, 3010, 2970, 2850, 2800, 1690, 1660, 1640, 1590, 1450, 1028, 1110, 700, 740

<sup>1</sup>H-NMR (ppm): 7.95-7.41(6H), 7.33-7.23(2H), 6.91-6.80(C=CH-), 6.65(N=CH-), 6.30-6.00(CH<sub>2</sub>=C), 3.71(CH<sub>3</sub>O-).

### Copolymerization

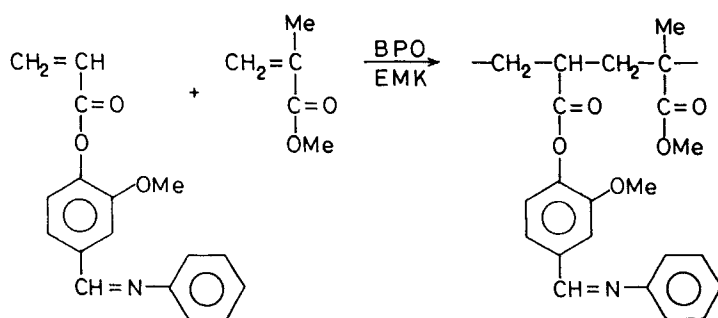
Predetermined quantities of MABPI and MMA with ethyl methyl ketone (EMK) and benzoyl peroxide were taken in a standard reaction tube (100 ml) and the mixture was purged with oxygen free nitrogen for 30 minutes. The tube was tightly sealed and immersed in a thermostated water bath maintained at 70 ± 1°C. To follow the copolymer equation, the conversions were restricted to less than 10%. After the required time, the reaction mixture was poured into excess methanol, the precipitated polymer was filtered off and purified by reprecipitation from dimethyl formamide (DMF) solution using methanol and finally dried in a vacuum oven at 50°C for 24 hours.

### Instrumentation

<sup>1</sup>H-NMR spectra of all the copolymer samples were run on a Hitachi 90 MHz NMR spectrometer. Spectra were recorded at room temperature for 15-20% (w/v) solutions in CDCl<sub>3</sub> and TMS was the internal standard. The IR spectra of the copolymers were recorded on a Hitachi 270-50 IR spectrophotometer using KBr pellets. The molecular weights  $M_w/M_n$  of the polymers were determined by Waters 501 Gel Permeation Chromatography equipment with an RI detector and calibrated with polystyrene standards and THF as the eluent. Viscometric measurements were made in dimethyl formamide (DMF) at 35°C with an Ubbelohde suspended level viscometer. Thermogravimetric analysis was carried out on Mettler 3000 thermal analyzer at a heating rate of 20°C per minute in air.

## RESULTS AND DISCUSSION

Seven copolymers of MABPI and MMA with different feed compositions were synthesized by radical solution polymerization in EMK using benzoyl perox-



SCHEME 1

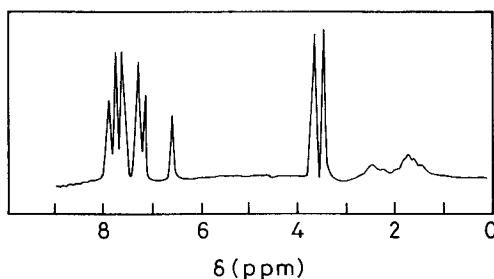
ide as initiator. Copolymerization was allowed to proceed to low conversion (less than 10%) in order to obtain polymer samples having a homogeneous composition as far as possible. The copolymer monomeric units are shown in Scheme 1.

### Characterization

The copolymers were soluble in chloroform, dimethylformamide, acetone, tetrahydrofuran, and dimethyl sulphoxide but insoluble in nonpolar solvents like benzene, xylene, and hexane as well as hydroxy-group containing polar solvents like water, methanol, and ethanol.

The IR spectrum of the copolymer reveals that the MABPI unit has more prominent features than the MMA. The peaks at  $1450\text{ cm}^{-1}$ ,  $1500\text{ cm}^{-1}$  and  $1590\text{ cm}^{-1}$  are due to aromatic  $> \text{C} = \text{C} <$  stretchings. Absorption at  $3010\text{ cm}^{-1}$  is assigned to aromatic unsaturated  $= \text{C}-\text{H}$  stretching. The CH stretching of the group  $-\text{CH}=\text{N}$  shows signal at  $2800\text{ cm}^{-1}$ . The ester carbonyl stretching is shown at  $1740\text{ cm}^{-1}$ . The  $\text{C}=\text{N}$  stretching due to imine group gives signal at  $1660\text{ cm}^{-1}$ . Bands at  $740\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$  may be due to the out of plane bending vibrations of the CH groups of benzene ring. The ether link due to OMe group and C-O link in the ester show signals at  $1050\text{ cm}^{-1}$  and  $1160\text{ cm}^{-1}$  respectively. The vibration due to the CH stretching of  $\text{CH}_3$  groups are shown at  $2960\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$ .

The proton NMR spectrum of the copolymer is shown in Figure 1. The chemical shift assignments for poly (MABPI-co-MMA) were based on the chemical shifts observed for the respective homopolymers. The aromatic protons of MABPI unit show signals between 7.34-7.20 ppm (2H) and between 7.98-7.43 ppm (6H). The OMe protons attached to benzene ring of MABPI unit gives signal at 3.72 ppm and that of MMA unit shows signal at 3.61 ppm. The methyne proton



**Figure 1.**  $^1\text{H-NMR}$  spectrum of poly(MABPI-co-MMA) system [0.50:0.50].

due to the  $-\text{CH}=\text{N}$  shows the characteristic signal at 6.66 ppm. The broad band at 1.98-1.5 ppm is due to the methylene ( $-\text{CH}_2-$ ) protons. The  $>\text{CH}-$  group shows a broad band between 2.332.05 ppm.

### Copolymer Compositions and Reactivity Ratios

Copolymer compositions were determined by  $^1\text{H-NMR}$  analysis. The assignment of the resonance peaks in the  $^1\text{H-NMR}$  spectrum allow for the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains. The signals between 7.34-7.20 ppm (2H) and between 7.987.43 ppm (6H) in Figure 1 correspond to aromatic protons of MABPI unit, and the signals at 3.72 ppm (3H) and 3.61 ppm (3H) are due to OMe protons attached to benzene ring of MABPI unit and OMe protons in MMA unit respectively. Hence the compositions of MABPI units in the MABPI-MMA copolymers were calculated by comparing the intensities of the aromatic protons of MABPI and the intensities of methoxy protons of MABPI unit and that of MMA unit in the copolymer.

The following formula was derived from copolymers consisting of both monomeric units. Let  $m_1$  be the mole fraction of MABPI and  $(1-m_1)$  that of MMA. There are eight aromatic protons and three methoxy protons in MABPI and three methoxy protons in MMA.

$$C = \frac{\text{Intensity of aromatic protons } (I_{Ar})}{\text{Intensity of methoxy protons } (I_{OMe})} = \frac{8 m_1}{3m_1 + 3(1-m_1)} \quad (1)$$

which on simplification gives,

TABLE 1. Composition Data for the Free Radical Copolymerization of MABPI with MMA in EMK solution at  $70 \pm 1^\circ\text{C}^a$

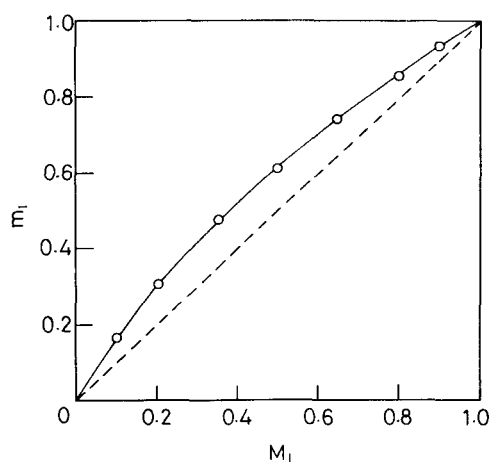
Feed Composition		Conversion %	Intensities of protons		$C = \frac{I_{Ar}}{I_{OMe}}$	Copolymer Composition	
$M_1$	$M_2$		$I_{Ar}$	$I_{OMe}$		$m_1$	$m_2$
0.10	0.90	8.82	1.10	2.40	0.4583	0.1718	0.8282
0.20	0.80	8.95	2.00	2.45	0.8163	0.3061	0.6939
0.35	0.65	7.89	4.50	3.55	1.2676	0.4753	0.5247
0.50	0.50	8.02	4.90	3.00	1.6333	0.6124	0.3876
0.65	0.35	9.66	5.00	2.55	1.9608	0.7353	0.2647
0.80	0.20	8.98	5.20	2.30	2.2609	0.8478	0.1522
0.90	0.10	9.52	5.60	2.25	2.4889	0.9333	0.0667

<sup>a</sup> $M_1$  and  $M_2$  are the mole fractions of MABPI and MMA respectively, in the feed.  $m_1$  and  $m_2$  are the mole fractions of MABPI and MMA respectively, in the copolymer.

$$m_1 = \frac{3C}{8} \quad (2)$$

Based on Equation 2, the mole fraction of MABPI in all copolymers was calculated by measuring the intensities of the aromatic proton signals and methoxy protons signals from the spectra of all copolymer samples. Table 1 shows the values of  $C$  and the corresponding mole fractions in the copolymers.

The normal kinetic behavior was determined by plotting the mole fractions of MABPI in the feed ( $M_1$ ) vs that the copolymer ( $m_1$ ) and the curve (Figure 2)



**Figure 2.** Composition diagram of MABPI-MMA copolymer system.

indicates that the composition of MABPI in the copolymer is always higher than that in the feed.

From the monomer feed ratios and the resultant copolymer compositions, the reactivity ratios of MABPI and MMA were evaluated by the application of methods of Fineman-Ross [16] and Kelen-Tüdös [17, 18]. No corrections for percentage conversion were made in utilizing conventional linear equation suggested by Kelen-Tüdös. The reactivity ratios obtained from the F - R (Figure 3) and K-T plots (Figure 4), are

$$\text{F-R method: } r_1 = 1.25 \pm 0.03 \text{ and } r_2 = 0.50 \pm 0.02$$

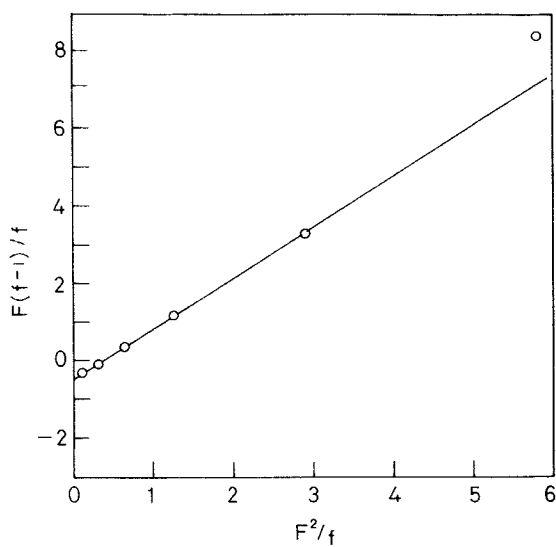
$$\text{K-T method: } r_1 = 1.28 \pm 0.02 \text{ and } r_2 = 0.50 \pm 0.02$$

Where  $r_1$  and  $r_2$  are the reactivity ratios relating to monomer 1 (MABPI) and monomer 2 (MMA), respectively. The difference between the two measurements is well within the experimental error. The value of  $r_1$  is more than 1 and that of  $r_2$  is less than 1 suggests the presence of a higher amount of MABPI units in the copolymer than in the feed.

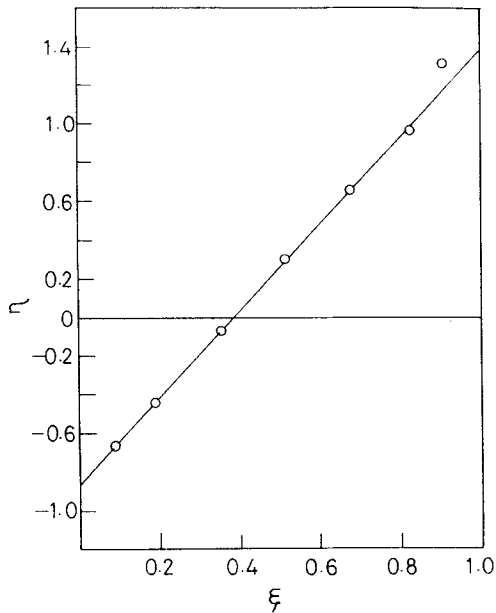
### Molecular Weights

The number-average, weight-average molecular weights ( $\bar{M}_w/\bar{M}_n$ ) and polydispersity index of homopolymers as well as five copolymer samples were determined by gel permeation chromatography, are presented in Table 2. The polydispersity index of poly (MABPI) and copolymer samples 2 and 3 are close to 1.5.





**Figure 3.** F-R plot for the determination of reactivity ratios of MABPI-MMA copolymer system.



**Figure 4.** K-T plot for the determination of reactivity ratios of MABPI-MMA copolymer system.

TABLE 2. Intrinsic Viscosities and Molecular Weights Data for the Copolymers of MABPI with MMA

Polymers	$M_1$	Molecular Weights			Intrinsic viscosity [ $\eta$ ], dL/g
		$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	
Poly(MABPI)	1.00	2.32	1.46	1.59	0.25
1	0.90	-	-	-	0.26
2	0.80	2.25	1.38	1.63	0.24
3	0.65	2.26	1.34	1.69	0.23
4	0.50	2.32	1.32	1.76	0.21
5	0.35	2.41	1.37	1.76	0.24
6	0.20	2.36	1.30	1.82	0.20
7	0.10	-	-	-	0.27
Poly(MMA)	0.00	2.43	1.32	1.84	-

$M_1$  is the mole fraction of MABPI in the feed.

and those of samples 4, 5, 6 and poly (MMA) are close to 2.0. The theoretical value of  $\bar{M}_w/\bar{M}_n$  for polymers produced via radical combination and disproportionation are 1.5 and 2.0, respectively [19]. In the homopolymerization of MMA, the radicals undergo termination mainly by disproportionation [20]. The values of  $\bar{M}_w/\bar{M}_n$  of these copolymers suggests a strong tendency for chain termination by disproportionation at high mole fractions of MMA and recombination at high mole fractions of MABPI in the feed.

TABLE 3. TGA Data of Homo and MABPI-co-MMA Copolymer System<sup>a</sup>

Polymers	Copolymer Compositions		IDT (°C)	Temperature (°C) at different weight loss (%)				
	m <sub>1</sub>	m <sub>2</sub>		10%	30%	50%	70%	90%
Poly(MMA)	0.00	1.00	244	280	319	350	393	444
Poly(MABPI-co-MMA)	0.61	0.39	256	294	331	388	456	556
Poly(MABPI)	1.00	0.00	269	305	344	431	506	625

<sup>a</sup>IDI - Initial Decomposition Temperature.

### Viscosity Measurements

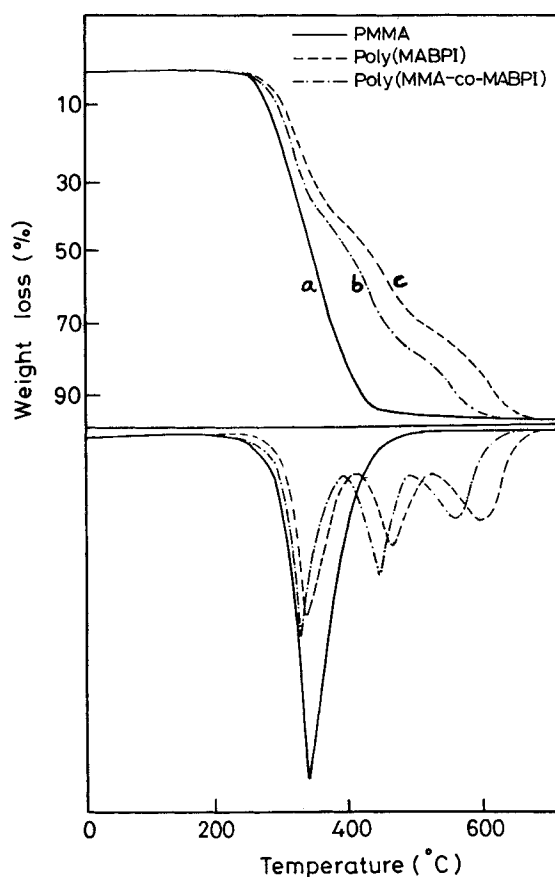
The intrinsic viscosity  $[\eta]$  were obtained by extrapolating  $\eta_{sp}/C$  to zero concentration. The data in Table 3 clearly indicates that the value of  $[\eta]$  is affected by the composition of the copolymer and the change is not uniform.

### Thermal Analysis

Thermogravimetric analysis curves of poly (MABPI) and poly (MABPI-co-MMA), and poly(MMA) are presented in Figure 5. Table 3 gives the results of decomposition temperature of polymers and its weight loss at various stages. The curves clearly show that poly(MMA) undergoes decomposition in a single stage and poly(MABPI-co-MMA) and poly(MABPI) undergo decomposition in three different stages. The initial decomposition temperatures of poly(MMA), poly(MABPI-co-MMA) and poly(MABPI) are 244°C, 256°C, and 269°C respectively. The stability of copolymers decreases with an increase of MMA in the copolymer chain.

## CONCLUSION

Poly(MABPI) and the copolymers of MABPI with MMA were synthesized in solution by free radical polymerization. Characterization of MABPI and



**Figure 5.** TGA curves of a) Poly(MMA), b) Poly(MABPI-co-MMA) [0.50:0.50], c) Poly(MABPI).

poly(MABPI-co-MMA) were performed with IR and  $^1\text{H-NMR}$  spectroscopic techniques. Copolymer compositions were calculated by both F-R and K-T methods and the values obtained ( $r_1 = 1.25, 1.28$  and  $r_2 = 0.50, 0.50$ ) are in good agreement. The  $r_1$  values of both methods are greater than 1, and this indicates that MABPI is more reactive than MMA. The copolymerization of MABPI with MMA ( $r_1 r_2 = 0.64$ ) resulted in random distribution of the monomeric units. GPC data showed the values of polydispersity index of poly(MABPI), poly(MABPI-co-MMA) and poly(MMA), suggesting a strong tendency for chain termination by disproportionation at high mole fractions of MMA and recombination at high mole fractions of MABPI in the feed. Thermogravimetric analysis results indicated that poly(MABPI) is thermally more stable than poly(MMA) and incorporation of

MMA reduced the thermal stability of poly(MABPI). Intrinsic viscosity values also proved the non uniformity of the copolymer.

## REFERENCES

- [1] O. Vogel, A. C. Albertsson, and Z. Janovic, *Polymer*, *26*, 1288 (1985).
- [2] J. A. Tortorello and D. J. Lukanich, (Desto Inc., U.S.); US Patent 4, 665, 146 (1987), Appl. 865, 784 (1986); *Chem. Abstr.*, *107*, P11 7048r (1987).
- [3] V. G. Syromyatnikov, V. V. Zagnii, R. N. Kuzmin, and E. L. Yatskiv, *Electron. Org. Mater.*, *210* (1985).
- [4] H. H. Hoerhold, *Z. Chem*, *12*, 41, (1972).
- [5] T. Kimura, (Nippon Telegraph and Telephone Public Corp., Japan), Kokai 75 78, 694, 3 pp, (1975); *Chem. Abstr.*, *83*, P 164854w, (1975).
- [6] A. Schmitter, J. Kiefer, and T. Haug (Ciba-Geigy A-G), Ger. Offen 2, 501, 110 (1975); Swiss Appl 572/74 (1974); *Chem. Abstr.*, *84*, p 45266 S (1976).
- [7] M. Tanaka and J. Kobayaski, (Agency of Industrial Sciences and Technology), Jpn. Kokai Tokkyo Koho JP 61, 257, 954 (1986), Appl 85/100, 877 (1985); *Chem. Abstr.*, *106*, p 175411u (1987).
- [8] S. Kato and S. Igami (Tokuyama Soda Co. Ltd.,) Jpn. Kokai Tokkyo Koho JP 61, 151, 161 (1986), Appl. 84/273, 294 (1984); *Chem. Abstr.*, *106*, p 138246y (1987).
- [9] A. S. Aswar and N. S. Bhave, *J. Indian. Chem. Soc.*, *74*, 75 (1997).
- [10] A. Schepartz and P. J. McDevitt, *J. Am. Chem. Soc.*, *111*, 5976 (1989).
- [11] Y. Fujii, K. Kikuchi, K. Matsutani, K. Ota, M. Adachi, M. Syoji, I. Haneishi, and Y. Kuwana, *Chem. Lett.*, *9*, 1487 (1984).
- [12] Osaka Gas Co. Ltd., Jpn. Kokai Tokkyo Koho JP 01, 118, 515 (1989); US Appl. 79, 665 (1987); *Chem. Abstr.*, *111*, P215126s (1989).
- [13] K. J. Ivin, S. Pitchumani, C. Rami Reddy, and S. Rajadurai, *J. Polym. Sci., Polym. Chem. Ed.*, *20*, 277 (1982).
- [14] J. C. J. F. Tacx, G. P. M. Vander Velden, and A. L. German, *Polymer*, *29*, 1675 (1988).
- [15] G. M. Stampel, R. P. Cross, and R. P. Maliella, *J. Am. Chem. Soc.*, *72*, 2899 (1950).
- [16] M. Fineman and S. D. Ross, *J. Polym. Sci.*, *5*, 259 (1950).
- [17] T. Kelen and F. Tüdös, *J. Macromol. Sci. Chem.*, *A9*, 1 (1975).

- [18] T. Kelen, F. Tüdös, and B. Tuucsanyl, *Polym. Bull.*, **2**, 71 (1980).
- [19] S. Teramachi, A. Hasegava, M. Akatsuka, A. Yamashita, and N. Takemoto, *Macromolecules*, **11**, 1206, (1978).
- [20] J. C. Bevington, H. W. Melville, and R. P. Jayalor, *J. Polym. Sci., Chem. Edn.*, **12**, 449 (1954).

Received September 25, 1997

Final revision received March 7, 1998