

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>

Copolymerization of 2-Vinylnaphthalene with Benzyudenemalononitrile

R. Vuković^a; V. Kurešcarevića^a; V. Srića^a; D. Fleš^a; F. Ranogajec^b

^a INA—Research and Development, Zagreb, Croatia ^b Ruder Boškarkovića Institute, Zagreb, Croatia

To cite this Article Vuković, R. , Kurešcarevića, V. , Srića, V. , Fleš, D. and Ranogajec, F.(1994) 'Copolymerization of 2-Vinylnaphthalene with Benzyudenemalononitrile', Journal of Macromolecular Science, Part A, 31: 12, 2001 – 2010

To link to this Article: DOI: 10.1080/10601329409350114

URL: <http://dx.doi.org/10.1080/10601329409350114>

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.

COPOLYMERIZATION OF 2-VINYLNAPHTHALENE WITH BENZYLIDENEMALONONITRILE

R. VUKOVIĆ, V. KUREŠEVIĆ, V. SRIĆA, and D. FLEŠ

INA – Research and Development
Zagreb, Croatia

F. RANOGAJEC

Ruder Bošković Institute
Zagreb, Croatia

ABSTRACT

Free radical-initiated copolymerization of 2-vinylnaphthalene (2-VNA) with benzylidenemalononitrile (BzMN) was performed in toluene to low conversion and to high conversion in a Calvet microcalorimeter. Under different monomer-to-monomer ratios in the feed at low and high conversion copolymerization, it was found that the usual terminal scheme of copolymerization fitted and that there was no significant kinetic effect of the penultimate unit. The reactivity ratios in low conversion copolymerizations were $r_1 = 0.85$ and $r_2 = 0$. In all cases, regardless to the monomer-to-monomer ratios in the feed, an excess of 2-VNA was present in copolymers. T_g values of copolymers are between 186 and 220°C, and they decrease with the increase of 2-VNA sequences in copolymer chains. Poly(2-VNA-co-BzMN) are film-forming materials which decompose by a one-step mechanism. Depending on the comonomers content in the copolymer, the weight loss is 50% between 325 and 360°C, and 90% at 400°C.

INTRODUCTION

In continuation of our studies on the preparation of copolymers of controlled steric and polar characteristics, we recently prepared copolymers of 2-vinylnaphthalene (2-VNA) with benzylidenemalononitrile (BzMN). The first comonomer contains a large bulky substituent, and although it is similar to styrene, due to lower localization energies it has a greater reactivity than styrene [1]. 2-VNA can homopolymerize by anionic, free-radical, and Ziegler-type catalysts. Benzylidenemalononitrile, on the other hand, does not homopolymerize but does readily copolymerize with various vinyl monomers. Kohn and coworkers have shown that in the copolymerization of vinyl acetate with BzMN, alternating copolymers are formed over a wide range of comonomer ratios in the feed [2], while in the copolymerization of styrene with BzMN up to low conversion, copolymers which contain an excess of styrene are formed [3]. In copolymerization of styrene with BzMN, Kohn and coworkers [3] found that the kinetics of copolymerization fitted the scheme proposed by Barb [4], which takes into account the effect of the penultimate unit.

In the present work we present our recent work on the copolymerization of 2-VNA with BzMN at various monomer ratios in the feed. The copolymerization was performed in toluene with AIBN as initiator up to low conversion by the "point-by-point" method or up to high conversion in a Calvet microcalorimeter.

EXPERIMENTAL

Monomers

2-Vinylnaphthalene (Aldrich Europe) was recrystallized from chloroform by the addition of petroleum ether (bp 30–60°C); mp 65–66°C (lit. [5] 65–66°C). Benzylidenemalononitrile was prepared in 90% yield by condensation of benzaldehyde with malononitrile in *tert*-amyl alcohol in the presence of piperidine as catalyst according to the method of Corson and Stoughton [6], mp 83–84°C (lit. [6] 83.5–84°C).

Copolymerization was performed in Pyrex test tubes in the presence of AIBN as initiator at different monomer-to-monomer ratios in the feed and at different total monomer concentrations. The copolymerizations were carried out at total monomer concentrations of 5.7 and 15.58 mol·L⁻¹, respectively; the compositions of the copolymers were evaluated from the nitrogen content.

Example of low conversion copolymerization: 0.05659 g AIBN was dissolved in 11 mL toluene, and 5.25 mL of this solution was poured into a Pyrex test tube which contained 5.6595 g 2-VNA. BzMN (5.6595 g) was dissolved in 5.25 mL toluene solution of AIBN. The desired amount of monomer solution was placed in the polymerization tube, degassed several times, sealed under nitrogen, and kept in a thermostated bath at 70°C until a yield of 5–15% was obtained. Copolymerization was stopped by cooling the reaction mixture. The content was diluted with 5 mL toluene and precipitated with xylene in the case of a low concentration of 2-VNA in the feed up to 5 mol·L⁻¹, while at higher molar concentrations of 2-VNA in the feed the copolymers were precipitated with hexane. The precipitated copolymers were filtered off, washed with methanol, and dried in vacuum for 60 hours at 90°C.

The copolymerization conditions and the properties of the copolymers are listed in Table 1.

The high conversion copolymerizations at different monomer-to-monomer ratios in the feed were performed in a Calvet microcalorimeter as previously described [7]. The copolymers were isolated in the same manner as described for the low conversion copolymerization.

Physicochemical Measurements

NMR spectra were obtained on a Varian EM 390 NMR spectrometer. An attempt was made to determine the equilibrium constant of the CT complex of 2-VNA with BzMN in CDCl_3 . The concentration of BzMN was $0.065 \text{ mol} \cdot \text{L}^{-1}$ with a chemical shift of 7.3 ppm, while the concentration of 2-VNA varied from 0.28 to

TABLE 1. Copolymerization of 2-Vinylmaphthalene (2-VNA) with Benzylidenemalononitrile (BzMN) in Toluene at 80°C , 0.5 wt% AIBN

Mole fraction in feed	2-VNA				Conversion, %			
	Mole fraction in copolymer				A	B	C	D ^b
	A, ^a 5 $\text{mol} \cdot \text{L}^{-1}$	B, ^a 7 $\text{mol} \cdot \text{L}^{-1}$	C, ^a 15.58 $\text{mol} \cdot \text{L}^{-1}$	D, ^b 5 $\text{mol} \cdot \text{L}^{-1}$				
0.1	—	—	0.522	—	—	—	8.30	—
0.2	0.585	0.550	0.563	—	4.12	3.93	9.83	—
0.3	—	0.640	0.623	0.540	—	6.96	7.36	51
0.4	0.615	0.635	0.633	—	9.98	7.95	11.65	—
0.5	—	0.650	0.650	0.550	—	9.01	11.82	65
0.6	0.720	0.700	0.668	—	13.92	9.33	13.50	—
0.7	—	0.730	0.680	0.633	—	9.66	11.88	82
0.8	0.725	0.780	0.731	—	13.80	11.28	13.39	—

Mole fraction in feed	$10^{-4} M_w$		$10^{-4} M_n$		$T_g, ^\circ\text{C}$		
	B	C	B	C	B	C	D
0.1	—	7.39	—	5.05	—	232	—
0.2	4.66	7.58	2.62	4.63	220	222	—
0.3	4.88	9.12	2.89	6.51	212	211	217
0.4	4.49	7.82	2.46	4.41	205	208	—
0.5	4.72	8.29	2.61	5.08	203	205	229
0.6	4.47	7.90	2.73	4.35	200	202	—
0.7	5.14	8.05	2.79	4.25	194	201	202
0.8	4.84	7.66	2.57	4.44	186	184	—

^aLow conversion copolymerization of 60–100 minutes.

^bHigh conversion copolymerization in Calvet microcalorimeter in 18 hours.

1.54 mol·L⁻¹. Molecular weights were determined on a Varian HPGPC Model 5800 using a set of 4 Styragel columns with THF as solvent. The average molecular weights were calculated by calibration with standard polystyrene of known molecular weights. Glass transition temperature measurements were carried out using a Perkin-Elmer Differential Scanning Calorimeter Instrument Model DSC-2. The scanning rate was 20°C/min in nitrogen. Thermogravimetric analysis was determined on a Perkin-Elmer TGS-2 thermogravimetric system in the temperature range of 60 to 600°C at a heating rate of 10°C/min in nitrogen.

RESULTS AND DISCUSSION

On mixing 2-VNA with BzMN, no change of color was observed. By applying the transformed Benesi-Hildebrand NMR procedure [8, 9], it was found that a slight change of chemical shifts occurred when the concentration of 2-VNA was increased in the mixture with BzMN. The calculated complexation constant has a very low value, $K = 0.02 \pm 0.01 \text{ L} \cdot \text{mol}^{-1}$, thus indicating that an extremely low concentration of complex exists in the comonomer mixture. It is of interest to mention that in several papers previously published from our laboratories it was shown that in spite of low complexation constants in the mixture of α -methylstyrene and *N*-substituted maleimides, all effects attributed to the participation of the CT complex were observed [10–13], and in all cases the alternating copolymers were obtained in free-radical initiated copolymerizations under different monomer-to-monomer ratios in the feed. It was therefore of interest to study the copolymerization of 2-VNA with BzMN and to compare the mechanism of copolymerization with previously described data for the copolymerizations of other monomers which form complexes with low complexation constants. It is also of interest to compare the mechanisms of copolymerization of 2-VNA with BzMN and with the mechanism of copolymerization of styrene with BzMN [14].

The copolymer composition obtained at different monomer-to-monomer ratios in the feed at different total monomer concentrations, T_g s, and molecular weights of copolymers are presented in Table 1.

As previously mentioned, BzMN does not homopolymerize under free-radical reaction conditions and has $r_2 = 0$. The copolymerization parameter $r_1 = k_{11}/k_{12}$ was calculated on the basis of the terminal model by Eq. (1) [2, 15, 16]:

$$y - 1 = r_1 x \quad (1)$$

where y denotes the ratio of the molar fraction in the copolymers (m_1/m_2) and x is the ratio of comonomers in the feed (M_1/M_2) with $M_1 = 2\text{-VNA}$ and $M_2 = \text{BzMN}$. From the plot of $y - 1$ against x in Fig. 1, r_1 was calculated as the slope of the straight line.

The reactivity ratios from Fig. 1 are $r_1 = 0.85$, $r_2 = 0$. It is of interest to mention that in contrast to the copolymerization of styrene with BzMN, where a strong penultimate unit effect exists [3], in copolymerization of 2-VNA with BzMN the effect of the penultimate unit was not evident. The r_1' is calculated by Eq. (2) [3, 14]:

$$y - 1 = r_1' x (1 + r_1 x) / (1 + r_1' x) \quad (2)$$

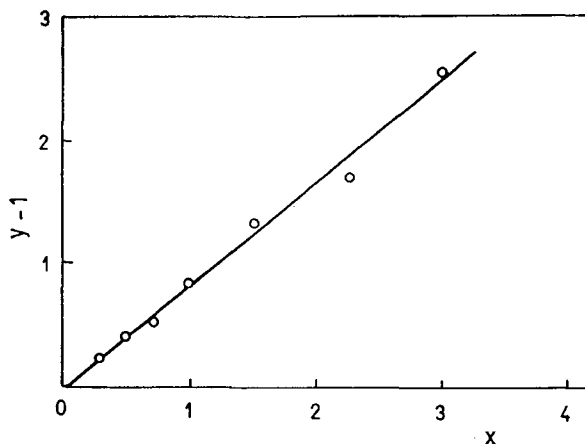


FIG. 1. Plot of $y - 1$ against x in the copolymerization of 2-VNA with BzMN in toluene at 80°C; 0.5 wt% AIBN; total monomer concentration in feed, $7 \text{ mol} \cdot \text{L}^{-1}$.

and has a value of $r_1' = 0.82$, similar to $r_1 = 0.85$, thus indicating that the effect of the penultimate units is not significant.

The dependence of the initial rate of copolymerization on the molar concentration of 2-VNA in the feed is presented in Fig. 2. It is evident that at low conversion copolymerization, the initial copolymerization rate increases with the increase of 2-VNA in the comonomer feed. Of interest is that in many copolymerizations of nonhomopolymerizable monomers with low complexation constants, the initial rate of copolymerization increases to a maximum at a nearly 1:1 initial comonomer mole ratio, and then the rate of copolymerization decreases [17, 18]. The copolymerization of 2-VNA with BzMN is also performed in a Calvet microcalorimeter up to high conversion. The time-conversion curves at the different molar ratios of

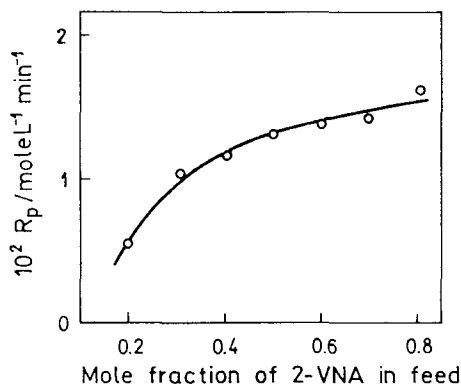


FIG. 2. Initial rate of copolymerization against molar concentration of 2-VNA in copolymerization with BzMN in toluene at 70°C; 0.5 wt% AIBN; total monomer concentration, $7 \text{ mol} \cdot \text{L}^{-1}$.

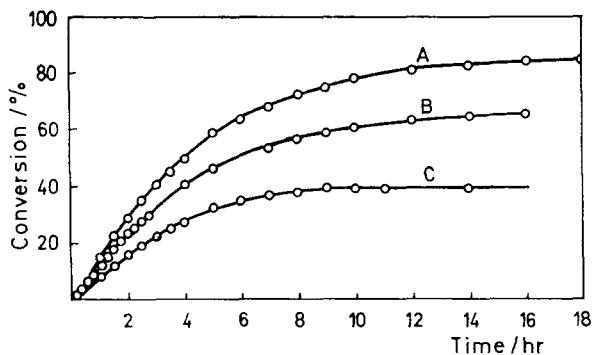


FIG. 3. Time-conversion curves in the copolymerization of 2-VNA with BzMN in toluene at 70°C, 0.5 wt% AIBN; total monomer concentration, 3 mol·L⁻¹. Mole fraction of 2-VNA, $f_1 = 0.7$ (A); 0.5 (B); 0.3 (C).

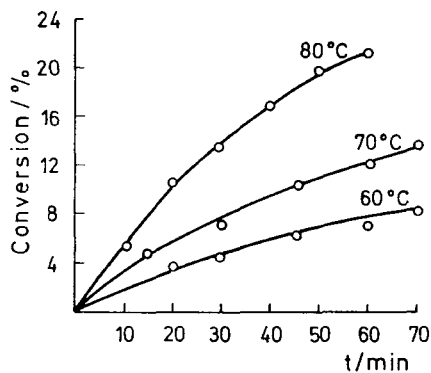


FIG. 4. Time-conversion curves in the copolymerization of 2-VNA with BzMN in toluene at 60, 70, and 80°C; 0.5 wt% AIBN.

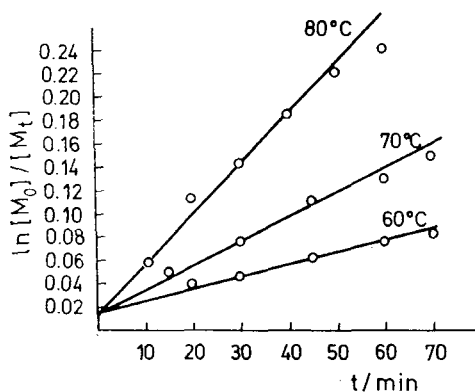


FIG. 5. First-order rate plots for the copolymerization of 2-VNA with BzMN in toluene at 60, 70 and 80°C; 0.5 wt% AIBN.

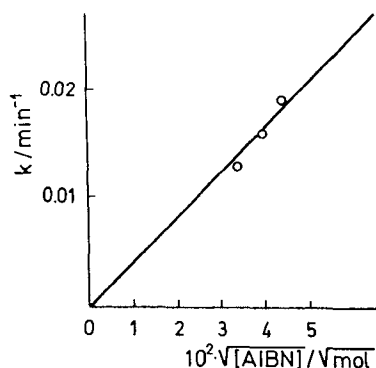


FIG. 6. Plot of rate constants vs $[AIBN]^{1/2}$ in the copolymerization of 2-VNA with BzMN in toluene at 70°C .

comonomers in the feed, shown in Fig. 3, also indicate that the yield of copolymer increases with an increase of 2-VNA in the feed.

The influence of temperature on the rate of conversion in the copolymerization of 2-VNA with BzMN is shown in Fig. 4. The linear relationship in the plot of initial monomer concentration over the monomer concentration at time t , against time, indicates that the copolymerization of 2-VNA with BzMN is a first-order reaction in 2-VNA, although it is difficult to distinguish between first- and second-order rate plots for low conversion copolymerization as shown in Fig. 5. Rate constants of the copolymerization at 60, 70, and 80°C , respectively, are determined

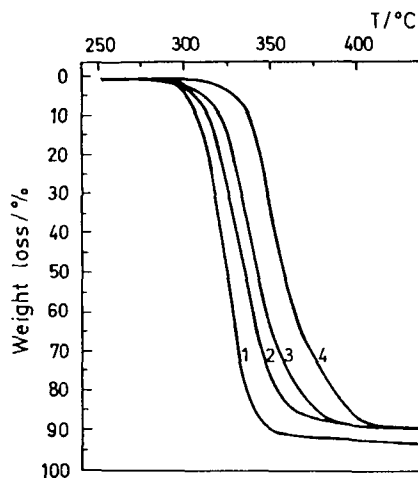


FIG. 7. Thermograms of decomposition of poly(2-VNA-co-BzMN) prepared at different monomer ratios in the feed; total monomer concentration $5\text{ mol}\cdot\text{L}^{-1}$, 70°C in toluene; 0.5 wt% AIBN; heating rate, $10^{\circ}\text{C}/\text{min}$ in N_2 ; mole fraction of 2-VNA in copolymer: (1) 58.5, (2) 61.5, (3) 72.0, (4) 72.5.

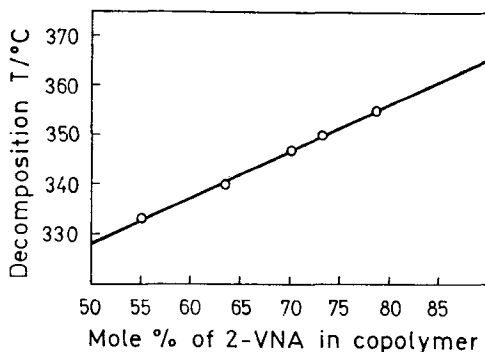


FIG. 8. Relationship between the temperature of maximal rate of decomposition in differential thermogravimetry and the mol% of 2-VNA in copolymer with BzMN; heating rate, 10°C/min in N₂.

as slopes of the straight lines in Fig. 5: $k_{60} = 0.001228 \text{ min}^{-1}$, $k_{70} = 0.002114 \text{ min}^{-1}$, $k_{80} = 0.00434 \text{ min}^{-1}$.

The activation energy was calculated by a graphical method using the Arrhenius equation: $E_A = \tan \alpha (R/0.4343)$, where E_A is the activation energy, $\tan \alpha$ is the slope of the straight line from the plot of log of rate constants against reciprocal absolute temperature of polymerization, and R is the gas constant: $E_A = 61.2 \text{ kJ} \cdot \text{mol}^{-1}$.

Similar to the findings previously described in the copolymerization of phenylvinyl alkyl ethers (alkyl = Me, Et, *sec*-Bu, *n*-Bu) with maleic anhydride [19], it was found that in the copolymerization of 2-VNA with BzMN, the rate of copolymerization was proportional to the square root of the AIBN concentration, thus indicating that bimolecular termination is involved (Fig. 6).

Poly(2-VNA-*co*-BzMN) is a thermostable film-forming material which decomposes by a one-step mechanism between 250 and 400°C (Fig. 7). The thermal stability of copolymers increases with an increase of 2-VNA in the copolymer and, as shown in Fig. 8, the temperature of the maximal rate of weight loss in differential thermogravimetry increases linearly with the increase of 2-VNA content in the copolymer. The data in Fig. 8 are very reproducible, and the ratio of comonomers in the copolymer can be calculated from the straight line in Fig. 8.

The glass transition temperatures of the copolymers are between 186°C for the copolymer which contains 78% of 2-VNA and 220°C for the copolymer which contains 55% of 2-VNA. In all cases, one well-defined T_g was obtained (Table 1).

CONCLUSION

1. From the results of free-radical initiated copolymerization of 2-VNA (M_1) with BzMN (M_2), monomer reactivity ratios as determined on the basis of the terminal model were $r_1 = 0.85$ and $r_2 = 0$.

2. No penultimate effect was observed in the copolymerization of 2-VNA with BzMN; $r_1' = 0.82$.
3. At low and high conversion copolymerization, the initial rate increases with an increase of 2-VNA in the copolymer feed.
4. The rate of copolymerization is proportional to the square root of the AIBN concentration.
5. Regardless to the ratio of comonomers in the feed, copolymers which contain an excess of 2-VNA approach alternating copolymers when $[2\text{-VNA}] \rightarrow 0$.
6. Copolymers decompose by a one-step mechanism between 250 and 400°C (TGA in N₂). T_g values are between 186 and 220°C, depending on the copolymer composition.

ACKNOWLEDGMENTS

This work was supported by two sponsoring agencies: the National Science Foundation of the USA and the Ministry of Science of the Republic of Croatia.

REFERENCES

- [1] F. Bahsteter, J. Smid, and M. Schwarz, *J. Am. Chem. Soc.*, **85**, 3909 (1963).
- [2] G. Kharas and D. H. Kohn, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 583 (1984).
- [3] M. Kreisel, V. Garbatsky, and D. H. Kohn, *J. Polym. Sci., Part A*, **2**, 105 (1964).
- [4] W. G. Barb, *J. Polym. Sci.*, **11**, 117 (1953).
- [5] M. M. Koton, *Ibid.*, **30**, 331 (1958).
- [6] B. B. Corson and R. W. Stoughton, *J. Am. Chem. Soc.*, **50**, 2825 (1928).
- [7] D. Fleš, F. Ranogajec, and R. Vuković, *Rad. Jugosl. Akad. Znan. Umjet., Kem.*, **425**(5), 19 (1986) (in English).
- [8] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1948).
- [9] M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, **68**, 811 (1964).
- [10] D. D. Fleš, R. Vuković, and V. Kurešević, *J. Macromol. Sci. – Chem.*, **A28**, 977 (1991).
- [11] D. Fleš, R. Vuković, F. Ranogajec, and D. Fleš, *Ibid.*, **A27**, 1621 (1990).
- [12] F. Ranogajec, D. D. Fleš, D. Hace, and R. Vuković, *Polym. Bull.*, **28**, 313 (1992).
- [13] D. D. Fleš, D. Hace, F. Ranogajec, and R. Vuković, *Ibid.*, **29**, 153 (1992).
- [14] E. T. Borrows, R. N. Haward, J. Porges, and J. Street, *J. Appl. Chem. (London)*, **5**, 379 (1955).
- [15] F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
- [16] T. Alfrey and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

- [17] I. Javni, D. Fleš, and R. Vuković, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 977 (1982).
- [18] K. G. Olson and G. B. Butler, *Macromolecules*, **17**, 2486 (1984).
- [19] R. Vuković, V. Kurešević, and D. Fleš, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 3835 (1979).

Received November 16, 1993

Revision received February 11, 1994