

Copolymers of vinylamine and vinylalcohol by acid hydrolysis of poly(N-vinyl-tert-butylcarbamate-co-vinylacetate) : evaluation of reactivity ratios

Citation for published version (APA):

Brouwer, W. M., Piet, P., & German, A. L. (1984). Copolymers of vinylamine and vinylalcohol by acid hydrolysis of poly(N-vinyl-tert-butylcarbamate-co-vinylacetate) : evaluation of reactivity ratios. *Journal of Polymer Science, Polymer Chemistry Edition*, 22(10), 2353-2362. <https://doi.org/10.1002/pol.1984.170221006>

DOI:

[10.1002/pol.1984.170221006](https://doi.org/10.1002/pol.1984.170221006)

Document status and date:

Published: 01/01/1984

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Copolymers of Vinylamine and Vinylalcohol by Acid Hydrolysis of Poly(*N*-Vinyl-*tert*- Butylcarbamate-co-Vinylacetate): Evaluation of Reactivity Ratios

W. M. BROUWER, P. PIET, and A. L. GERMAN, *Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands*

Synopsis

Copolymers of vinylamine and vinylalcohol were prepared by hydrolysis of poly(*N*-vinyl-*tert*-butylcarbamate-co-vinylacetate) in 1:1 v/v % ethanol/HCl mixtures at room temperature. Reactivity ratios of the monomers *N*-vinyl-*tert*-butylcarbamate (1) and vinylacetate (2) were calculated from monomer feed and copolymer composition data, according to the methods of Fineman-Ross and Kelen-Tüdös, yielding $r_1 = 1.14 \pm 0.05$, $r_2 = 0.47 \pm 0.07$, and $r_1 = 1.12 \pm 0.07$, $r_2 = 0.46 \pm 0.03$, respectively. From these values the average sequence length distribution of monomer units was derived showing that in the reaction of *N*-vinyl-*tert*-butylcarbamate and vinylacetate nearly Bernoullian (i.e., purely random) copolymers are formed, with a slight tendency toward alternation.

INTRODUCTION

The polymeric amine with the simplest chemical structure is undoubtedly poly(vinylamine) and although its synthesis is rather laborious, it can be prepared according to one of the synthetic routes already known.¹⁻⁵

Some important features of these polymers are their water solubility, complexation properties toward transition metal ions,⁶ rather high basicity of the amine groups ($\text{pK}_a(-\text{NH}_3^+) \approx 9$),⁷ and the capability of easy reaction with all kinds of electrophilic compounds, such as dyes.⁴ The pH-dependent basicity of amine groups is of fundamental scientific interest.⁸

In our laboratory poly(vinylamine) is being used as a functional polymeric ligand of a thiol oxidation catalyst. Application of this polymeric base instead of NaOH was found to increase catalytic activity 50-fold.⁹ It appeared from viscosity,¹⁰ pH,¹¹ and kinetic¹² measurements that the amine group basicity, polymer charge, and conformation largely affected catalytic activity. Combination of these properties with other desirable functionalities can be achieved by appropriate copolymerization. Selection of the synthetic route will depend on the nature of the comonomer.

Copolymers of vinylamine and a suitable uncharged comonomer seem to offer the opportunity to investigate the effect of base group density within the polymer chain on catalytic activity.

For this purpose copolymers with either randomly distributed vinylamine units or alternating monomer units are preferred to block copolymers.

Until now, to our knowledge, the synthesis of only two water-soluble vinyl

copolymers containing vinylamine has been reported: copolymers of vinylamine with sodium vinylsulfonate, containing cationic and anionic functionalities in water,¹³ and copolymers of vinylamine with vinylalcohol, containing only cationic functionalities. The latter copolymers were prepared first by Nikolayev¹⁴ starting from copolymers of vinylphthalimide and vinylacetate, which could be aminolyzed and hydrolyzed, respectively, with hydrazine hydrate. Decomposition of the formed phthalylhydrazide salt of vinylamine was achieved in hydrochloric acid according to the method of Reynolds and Kenyon.¹ Very recently, a new way of preparing copolymers of vinylamine and vinylalcohol, by acid hydrolysis of copolymers of *N*-vinyl-*tert*-butylcarbamate (NVTBC) and vinylacetate (VAc), based on the Hart synthesis of polyvinylamine¹⁵ was outlined briefly by Bloys van Treslong and Jansen.¹⁶ The synthetic route they described is an important contribution to making these copolymers more accessible to further investigations. Unfortunately, little copolymerization data were presented, thus prohibiting accurate calculation of the reactivity ratios of the pre-monomers. Therefore, we followed their preparation method successfully (with minor modifications) and determined the copolymer reactivity ratios of the monomers from complete data to get insight into the randomness of these very hygroscopic copolymers.

EXPERIMENTAL

Synthesis of the Pre-Copolymers

NVTBC was synthesized according to the Hart method,¹⁵ with some minor modifications.¹⁷ After drying thoroughly, the white, powdery NVTBC was purified by sublimation at 54°C at 1 kPa pressure. Because of the highly poisonous character of NVTBC—*in aquo* the toxic hydrolysis product ethylenimine is formed—all manipulations with this reagent were carried out under an efficient fume hood. VAc (kindly provided by DSM) was vacuum distilled before use.

Copolymerization of NVTBC and VAc was carried out in benzene (Merck *pro analysi*, dried on CaH₂) at 60°C for 6 h with α , α' -azoisobutyronitrile as initiator under nitrogen. The pre-copolymers were isolated by precipitating the reaction product in a 20-fold excess of ice-cold *n*-hexane. After drying, the copolymers were purified by redissolution in toluene and precipitation in *n*-hexane, followed by washing with *n*-heptane (*pro analysi*) to remove residual initiator. The purified copolymers (I) (Scheme 1) were dried at 0.1 Pa, at 35°C.

Number average molecular weights (\overline{M}_n) were determined in toluene at 37°C with a Hewlett-Packard 502 high-speed membrane osmometer, (\overline{M}_n) in the range of 30,000 to 75,000 g mol⁻¹.

The molar fraction of NVTBC units in the copolymer, α , was calculated from either the nitrogen content, obtained from elemental analysis, or the relative peak intensity of the methyl protons of the *tert*-butyl group in the ¹H-NMR spectrum. (Although the methylene peaks (a and b in Fig. 3) are fully separated, these peaks were nevertheless considered too small for proper analysis.)

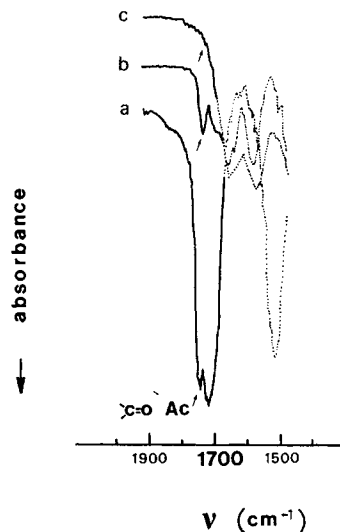


Fig. 1. IR spectra of (I) ($\alpha = 0.56$) after hydrolysis during (a) 0 h, (b) 20 h, (c) 48 h. Arrows indicate the carbonyl group of the acetate moiety at 1750 cm^{-1} .

Analysis

Samples for IR spectra were prepared by evaporation of some drops of a methanolic solution of (III) on a KBr disk. Polymers (I) were dispersed in a KBr disk. Characteristic absorptions of (III) occurred at 3400 cm^{-1} (OH, NH_2), 2950 cm^{-1} (CH_2 , CH), 1620 cm^{-1} (NH_2), 1470 cm^{-1} (CH_2 , CH), 1100 cm^{-1} (CH), and 850 cm^{-1} (C-C).

Potentiometric titration of copolymers (III) was performed with HCl (0.03*N*) in the presence of 2*M* NaCl. Titration times were not shorter than 20 min, for reasons of reproducibility.

RESULTS AND DISCUSSION

Features of Synthesis

Complete hydrolysis of poly(*N*-vinyl-*tert*-butylcarbamate-co-vinylacetate) could be obtained after 48 h of reaction in a mixture of 1:1 v/v % ethanol/concentrated HCl at room temperature. The hydrolysis of *tert*-butylcarbamate is completed within $\frac{1}{2}$ h,⁵ but the hydrolysis of the acetate is rather slow under these conditions. The rate of hydrolysis of the acetate group could be followed by monitoring the decrease in the $-\text{C}=\text{O}$ band intensity at 1750 cm^{-1} in the IR spectra of the copolymers (Fig. 1). It is shown that after 20 h of reaction (b in Fig. 1) almost all VAc is hydrolyzed and after 48 h the reaction is complete.

Copolymers (II) were only soluble in water, but the deprotonated forms (III) were very soluble in both water and the lower alcohols in agreement with Nikolayev.¹⁴

Basicity of the Amine Groups

Copolymers (III) were subjected to potentiometric titration experiments with HCl in 2*M* NaCl. The results are shown in Figure 2, revealing that

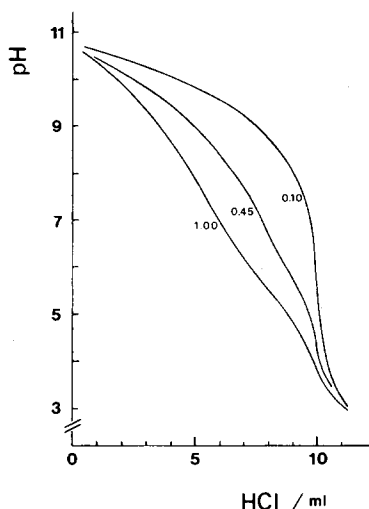


Fig. 2. Potentiometric titrations of copolymers (III) with 0.03*N* HCl in 2*M* NaCl. Solutions contain 0.3 mmol of amine groups. α values are given in the figure.

the individual amine groups possess a higher basicity as the amine group content in the copolymers is lower. This behaviour can be explained by assuming a decreased nearest neighbour interaction when the amine groups find themselves more isolated in the polymer chain at low values. On the grounds of these experimental observations, copolymers with a high degree of randomness or alternation are expected to be formed. In the following section this inference will be confirmed by measuring the copolymer reactivity ratios. The titration behaviour, shown in Figure 2, is in qualitative agreement with the titration experiments performed by Bloys van Treslong and Jansen¹⁶ and by Kimura et al.¹⁸ on copolymers (III) prepared according to the Hart method⁵ and the Nikolayev method,¹⁴ respectively.

Reactivity Ratios of NVTBC and VAc in Benzene

The dependence of copolymer composition on the monomer feed was evaluated for initial molar monomer feed ratios, q_0 , in the range 0.05 to 4. Total conversion was mostly 15% but never exceeded 30%, to avoid large shifts in the monomer feed ratio.

Copolymer compositions were calculated from elemental analysis (C,H,N) of the purified, dried copolymers (I). For some of these copolymers the composition was determined from the methyl proton peak intensity of the tert-butyl group of (I) in the ¹H-NMR spectrum (shown in Fig. 3 for $\alpha = 0.43$). In Table I values of α , obtained from NMR and elemental analysis data, are given, showing that within experimental error the NMR data are in good agreement with the elemental analysis results.

The reactivity ratios of monomers (1) and (2) have been evaluated according to the methods of Fineman and Ross¹⁹ and Kelen and Tüdös.²⁰ These methods were selected on the grounds of experimental convenience, since in the present case copolymer compositional analysis appeared to be available much more easily and accurately than monomer feed data during the polymerization.

In the Fineman-Ross method the parameters $F = (\bar{q})^2/x$ and $G = \bar{q}(x -$

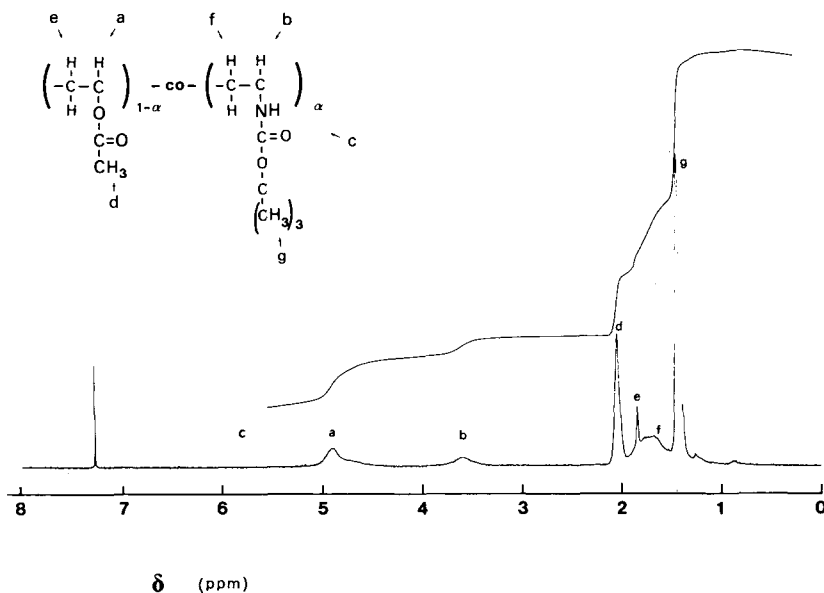


Fig. 3. $^1\text{H-NMR}$ spectrum of (I) ($\alpha = 0.43$) in CDCl_3 with CHCl_3 as internal standard. Peaks correspond to the hydrogen atoms indicated.

$1)/x$ are evaluated, where \bar{q} = the average ratio of molar concentrations of monomers (1) and (2) and x = the molar ratio of these monomers in the copolymers. This analysis is shown in Figure 4. In the calculations, q_0 instead of \bar{q} was used, since simulation experiments²¹ show that for the present pair of r values and degree of conversion any possible deviations of these r values, introduced by substituting q_0 for \bar{q} , will be within the error intervals given for the Fineman-Ross method. Moreover, in Figure 4

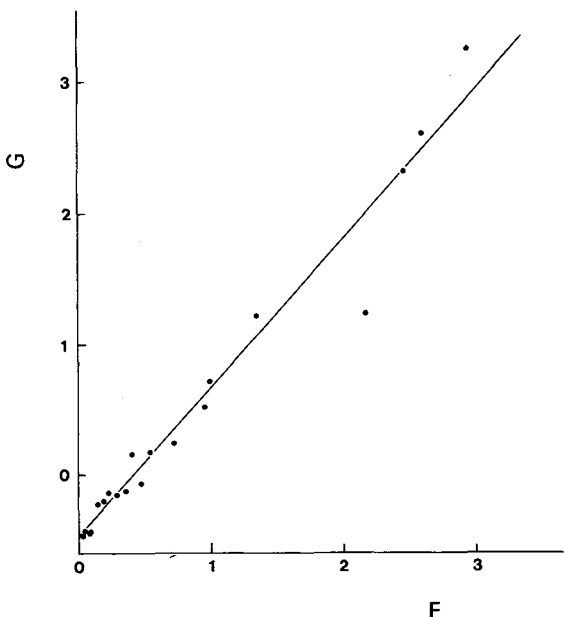


Fig. 4. Fineman-Ross plot; the intercept gives $-r_2$ and the slope gives r_1 .

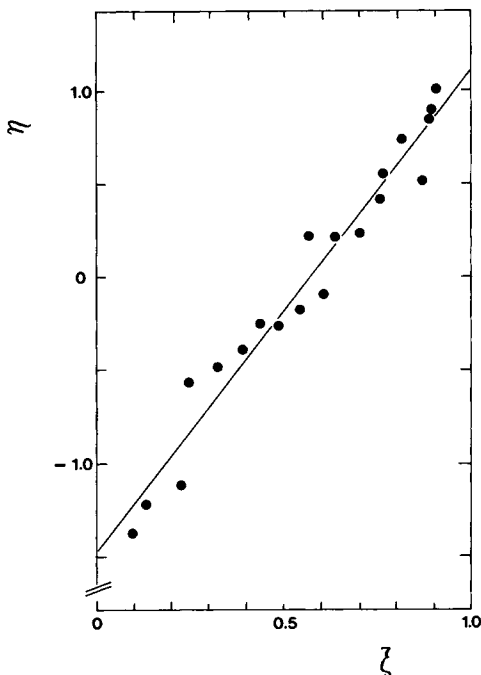


Fig. 5. Kelen-Tüdös plot; the intercept at $\xi = 0$ gives $-r_2/\beta$, and the intercept at $\xi = 1$ gives r_1 . $\beta = 0.31$.

the experimental points derived from relatively high conversion (30%) experiments do not deviate significantly more from the drawn linear fit than do the points pertaining to lower conversion experiments. In the method designed by Kelen and Tüdös for low conversion, the experimental points are symmetrized by introducing the parameter $\beta = (F_{\min}F_{\max})^{1/2}$ in the dependent variables $\xi = F(\beta + F)$ and $\eta = G(\beta + F)$. According to the latter method, data contained in Figure 4 were replotted in Figure 5. Reactivity ratios calculated from Figures 4 and 5 are given in Table II, which shows that the results of both methods are in good agreement. Obviously, the effect on r_1 and r_2 of symmetrization of the experimental points as occurs in the Kelen-Tüdös method is negligible. The values of r_1 and r_2 found here (1.14 ± 0.05 and 0.47 ± 0.05 , respectively) deviate considerably from the values recently reported by Bloys van Treslong and Jansen,¹⁶ viz., 1.8 ± 0.2 and 0.76 ± 0.11 , respectively.

TABLE I
Comparison of Copolymer Compositional Determination by Elemental Analysis (C,H,N) and ¹H-NMR

Mole fraction of NVTBC in monomer feed	α^a (CHN)	α^b (¹ H-NMR)
0.80	0.84 ± 0.05	0.83 ± 0.06
0.59	0.67 ± 0.04	0.74 ± 0.05
0.31	0.43 ± 0.03	0.44 ± 0.03
0.18	0.33 ± 0.02	0.30 ± 0.02
0.13	0.20 ± 0.01	0.21 ± 0.02

^a Nitrogen content of (I) has been used.

^b Methyl proton peak intensity of the tert-butyl group in (I) has been used.

TABLE II
 Reactivity Ratios of NVTBC and VAc in Benzene, Calculated According to the Methods of
 Fineman and Ross (F-R) and Kelen and Tüdös (K-T)

Method of data analysis	r_1	r_2
F-R	1.14 ± 0.05	0.47 ± 0.07
K-T	1.12 ± 0.07	0.46 ± 0.03

However, their experimental points do not seriously conflict with ours as would appear from plotting their data in Figure 4. The main reason for the discrepancy in the reactivity ratio values is that although the latter authors used a calculation method essentially the same as the Fineman-Ross procedure¹⁹ only a few experimental points within a very narrow range of monomer feed ratios were available, not enough for determining the reactivity ratios sufficiently accurately.

Summarizing, more accurate reactivity ratios will be obtained when using more experimental data obtained from copolymerization experiments over a wider range of monomer feed compositions. If possible, the copolymer compositional analysis should be confirmed by a second technique. On these grounds, we believe our present data to be the more reliable.

Sequence Distribution

The distribution of monomer units in the copolymer is directly related to the reactivity ratios, the latter being measures of the probability of occurrence of homogeneous sequences of either monomer unit. To gain insight into the randomness of the monomer unit distribution along the polymer chain, the relative numbers of amine-amine, amine-alcohol, and alcohol-alcohol neighbouring groups as well as the number average sequence length of either monomer have been calculated²² and compared with a situation of Bernouillian distributed, i.e., purely randomly, sequenced monomer units. In Table III the results are listed for a copolymer with $\alpha = 0.43$. A more sensitive indicator of deviations from the Bernouillian distribution is the so-called monomer dispersity index, MD, which is defined as $100/\bar{l}$, where \bar{l} is the number average sequence length.²³ An MD value

TABLE III
 Calculated Diad Abundance and Number Average Sequence Length in One of the Present
 Copolymers as Compared with a Hypothetical Bernouillian-Type Copolymer ($\alpha = 0.43$)

	Present copolymer ^a		Perfectly Bernouillian sequenced copolymer
Diad abundance (%) ^b	11	15	18
	12 + 21	57	49
	22	29	32
Sequence length ^b	\bar{l}_1	1.51	1.75
	\bar{l}_2	2.00	2.33

^a $r_1 = 1.12$, $r_2 = 0.46$, $q_0 = 0.46$.

^b 1 = Vinylamine unit, 2 = vinylalcohol unit.

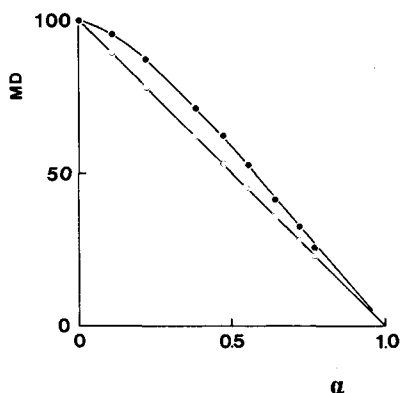


Fig. 6. Monomer dispersity of vinylamine units versus α . (●) In the presently synthesized copolymers, (○) in hypothetical Bernoullian-type copolymers.

of 100 would indicate that all vinylamine units occur isolated in alcohol-amine-alcohol sequences. Any value below 100 is indicative of the occurrence of contiguous amine-amine units.

In Figure 6, values of MD of vinylamine units for copolymers formed according to the present pair of r values as well as for a hypothetical perfect Bernoullian-type copolymer are plotted versus the copolymer composition α . From the calculations (Table III and Fig. 6) it may be concluded that in the reaction of NVTBC with VAc random copolymers are formed with a slight tendency toward alternation. These copolymers are therefore eminently suitable as polymeric ligands in a study on the relation between base density within a polymeric thiol oxidation catalyst and catalytic activity. The results of this study will be reported separately.

The authors would like to thank Mr. W. J. Kingma for his assistance in the NVTBC synthesis, Ir. F. L. M. Hautus for his support in the evaluation of reactivity ratios, Mr. H. Eding for performing the elemental analysis, and Dr. Ir. J. W. de Haan and Mr. L. J. M. van de Ven for the NMR results.

References

1. D. D. Reynolds and W. O. Kenyon, *J. Am. Chem. Soc.*, **69**, 911 (1947).
2. E. Bayer, K. Gecheler, and K. Weingärtner, *Makromol. Chem.*, **181**, 585 (1980).
3. H. Tanaka and R. Senju, *Bull. Chem. Soc. Jpn.*, **19**, 2821 (1976).
4. D. J. Dawson, R. D. Gless, and R. E. Wingard, Jr., *J. Am. Chem. Soc.*, **98**(19), 5996 (1976).
5. R. Hart, *Makromol. Chem.*, **32**, 51 (1959); and *J. Polym. Sci.*, **29**, 629 (1958).
6. Ph. Teyssié, C. Decoene, and M. T. Teyssié, *Makromol. Chem.*, **84**, 51 (1965).
7. C. J. Bloys van Treslong and A. J. Staverman, *Recl. Trav. Chim. Pays-Bas*, **97**(1), 13 (1978).
8. A. Katchalsky, J. Mazur, and P. Spitnik, *J. Polym. Sci.*, **23**, 513 (1957).
9. J. H. Schutten and J. Zwart, *J. Mol. Catal.*, **5**, 9 (1979).
10. W. M. Brouwer, P. Piet, and A. L. German, *Polym. Commun.*, **24**, 216 (1983).
11. W. M. Brouwer, P. Piet, and A. L. German, *Pol. Bull.*, **8**, 245 (1982).
12. W. M. Brouwer, P. Piet, and A. L. German, *J. Mol. Catal.*, **22**, 297 (1984).
13. M. Kronstadt, D. J. Dawson, and P. L. Dubin, *Polym. Prepr. Am. Chem. Soc.*, **19**(1), 280 (1978).
14. A. F. Nikolayev, S. N. Ushakov, L. P. Vishnevetskaya, and N. A. Voronova, *Vysokomol. Soyed.*, **5**(4), 547 (1963); English translation: *Polym. Sci. USSR*, **4**, 1221 (1963).

15. A. R. Hughes and T. St. Pierre, *Macromol. Synth.*, **6**, 31 (1977).
16. C. J. Bloys van Treslong and B. J. Jansen, *Eur. Polym. J.*, **19**, 131 (1983).
17. W. M. Brouwer, P. Piet, and A. L. German, *Makromol. Chem.*, **185**, 363 (1984).
18. K. Kimura, Y. Inaki, and K. Takemoto, *Makromol. Chem.*, **176**, 2225 (1975).
19. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
20. T. Kelen and F. Tüdös, *J. Macromol. Sci. Chem. A*, **9**, 1 (1975).
21. F. L. M. Hautus, H. N. Linssen, and A. L. German, *J. Polym. Sci. Polym. Chem. Ed.*, in press.
22. H. J. Harwood and W. M. Ritchey, *J. Polym. Sci. Polym. Lett. Ed.*, **2**, 601 (1964).
23. E. T. Hsieh and J. C. Randall, *Macromolecules*, **15**, 1402 (1982).

Received October 13, 1983

Accepted February 21, 1984