*Macromolecules* 1984, *17*, 611-614

# Unperturbed Dimensions of Poly[bis(phenyl-*n*-alkyl) itaconates]†

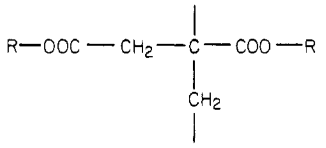
**Jovan Veličković* and Jovanka Filipović**

*Faculty of Technology and Metallurgy, Department of Organic Chemical Technology, Karnegijeva 4, YU-11000 Belgrade, Yugoslavia.* *Received July 12, 1983*

ABSTRACT: Poly(dibenzyl itaconate), poly[bis(phenylethyl) itaconate], poly[bis(phenyl-*n*-propyl) itaconate], and the previously described poly(diphenyl itaconate) are considered as a polymer homologous series in which methylene groups are introduced stepwise into both substituents of the vinylidene repeat unit. The polymers were synthesized radically and then fractionated, and from the intrinsic viscosities and molecular weights of the fractions, the Kuhn–Mark–Houwink–Sakurada relations in toluene at 25 °C were established. The observed decrease of the exponent $a$ reflects the increase of the paraffinic character. From extrapolations of viscosities to Θ-conditions according to the methods of Kurata and Stockmayer, Stockmayer and Fixman, and others, $K_\Theta$ was estimated and $\sigma$-values from 2.60 to 2.81 were calculated for the series, indicating an increase of hindrance to rotation. The results are discussed in terms of chemical composition of the repeat units and compared with those for similar polymer homologous series.

## Introduction

Recently, attention has been devoted to the investigation of polymers of itaconic acid derivatives, from both a fundamental and a practical point of view. With properties similar to those of the structurally related poly(acrylates) and poly(methacrylates), interest for these products is increasing as the acid and several other reactants for the production of monomers can be obtained by fermentation processes of agricultural wastes.[1] Poly(itaconates) were first reviewed by Tate.[2] The latter work is in part contained in papers by Veličković et al.,[3–6] dealing with problems of synthesis and dilute solution properties and with copolymers,[7] in publications of Cowie et al.,[8–10] referring to solid-state properties, and in a recent monograph.[11] One of the objects of all these investigations was the study of the influence of the size and type of the two structurally similar ester substituents of the repeat unit, represented as



$$R{-}OOC{-}CH_2{-}\overset{|}{\underset{\underset{|}{CH_2}}{C}}{-}COO{-}R$$

on polymer properties. The present investigation was inspired by research on poly(diphenyl itaconate)[6] (PDFI), the first systematically described aromatically substituted poly(itaconate). By introducing methylene groups between the phenyl and ester function in the substituents, one should be able to generate a polymer homologous series in which the properties should change stepwise and correlate with those of PDFI and also other poly(itaconates). In this work attention is focused on polymer unperturbed dimensions. The three polymers investigated are presented in Table I. Excluding patent literature, the polymers of this investigation were described only with respect of their glass transition temperatures[8] and polymer cohesive energy densities.[12] No data regarding molecular weight determinations and unperturbed dimensions have been published.

## Experimental Section

All the methods for monomer and polymer syntheses were essentially the same as described for poly(di-*n*-alkyl itaconates).[3] Synthesis-grade itaconic acid and aromatic alcohols (products of BDH) of at least 99% purity were used for the preparation of monomers. Commercially available $\alpha,\alpha'$-azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol before use. Polymer purification and fractionation was performed with high-purity methanol and benzene; *n*-butanone and toluene for polymer characterization were distilled before use.

**Monomer and Polymer Syntheses.** The monomers were obtained by direct esterification of itaconic acid with a 50–60% molar excess of alcohol in the presence of small amounts of *p*-toluenesulfonic acid catalyst. After the theoretical amount of water was separated, the reaction mixture was neutralized, washed, and dried, and the monomer was separated by vacuum distillation.

The monomers were polymerized radically with 0.1–0.5 wt % AIBN in vacuum-sealed glass tubes at temperatures of 40–80 °C over the course of several hours to 2–3 days until a solidification of the oily monomer in the tubes was observed. Both temperature and initiator concentration were selected by experience in order to obtain polymers of suitable $\bar{M}_w$ for further investigation. The reaction mixture was then dissolved in benzene, precipitated several times to remove unreacted monomer, and dried to constant weight under reduced pressure.

**Polymer Fractionation.** The polymers were fractionated on a Baker–Williams column, supported on acid-washed glass beads and kept at 40.0 °C at the top and 18.0 °C at the bottom, of 1300-mm height. The starting concentrations of benzene/methanol solvent and nonsolvent were estimated from critical volume fractions of methanol $\varphi_2$ necessary to produce a first and maximum turbidity when titrating a 0.1 wt % solution of polymer in benzene with methanol. An increasing solvent concentration gradient was established by continuously introducing the solvent into a stirred 500-mL nonsolvent vessel at the top of the column. Amounts of 2.5–3 g of polymer were fractionated with about 3 L of solvent and nonsolvent into 30–40 fractions, which were occasionally combined to obtain sufficient material for light scattering and viscosity determination.

**Intrinsic Viscosities ([$\eta$]).** These were obtained in a dilution-type viscometer in toluene at 25.00 ± 0.05 °C without correction for kinetic effects; [$\eta$] are expressed in cm$^3$/g.

**Refractive Index Increments ($\nu$).** $\nu$-values, expressed in cm$^3$/g, were obtained on a Brice-Phoenix Model 2000 differential refractometer at 20 °C in *n*-butanone with light of 436 nm.

**Weight-Average Molecular Weights ($\bar{M}_w$).** Molecular weights were obtained by light scattering measurements of a 1% polymer solution and of three dilutions in *n*-butanone on a Brice-Phoenix light scattering instrument Model 2000 at ambient temperature at eight different scattering angles within the range 35–125° according to the method of Zimm.[13]

## Results and Discussion

**Monomer and Polymer Syntheses.** All monomers are viscous pale yellow oils. Among the polymers PDBzI is brittle and glassy at ambient temperature and crushes easily into small particles, while PDEFI and PDPFI are transparent and film forming. Elemental analyses of both monomer and polymer were close to those calculated. [$\eta$] increase with decreasing polymerization temperature and initiator concentration and spread in the range from 12.8

---

† This paper is dedicated to Walter Stockmayer on the occasion of his 70th birthday.

0024-9297/84/2217-0611$01.50/0

Table I
Poly[bis(phenylalkyl)itaconates] Investigated

| corresponding monomer | R group | polymer abbrev | monomer mol wt |
|---|---|---|---|
| dibenzyl itaconate | $CH_2C_6H_5$ | PDBzI | 310 |
| bis(phenylethyl) itaconate | $(CH_2)_2C_6H_5$ | PDEFI | 338 |
| bis(phenyl-*n*-propyl) itaconate | $(CH_2)_3C_6H_5$ | PDPFI | 366 |

Table II
Details of Monomer and Polymer Properties

| polymer | monomer ref index $n^{20}{}_D$ | monomer density, $cm^3/g$ | polymer density, $cm^3/g$ | $\nu$, $cm^3/g$ (*n*-butanone) |
|---|---|---|---|---|
| PDBzI | 1.5505 | 1.158 | 1.23 | 0.183 |
| PDEFI | 1.5447 | 1.119 | 1.20 | 0.180 |
| PDPFI | 1.5352 | 1.092 | 1.17 | 0.173 |

Table III
Molecular Weights and Limiting Viscosities of PDEFI

| $\bar{M}_w$ | $[\eta]$ (25 °C, toluene) | $\bar{M}_w$ | $[\eta]$ (25 °C, toluene) |
|---|---|---|---|
| 90 200 | 10.65 | 243 700 | 19.20 |
| 125 600 | 12.30 | 275 000 | 22.60 |
| 145 800 | 13.90 | 343 400 | 25.60 |
| 196 000 | 16.35 | 453 600 | 29.25 |

to 60.4 $cm^3/g$. IR spectra of PDBzI and PDEFI from this investigation are included in the Hummel/Scholl atlas.[14] Other significant characteristics of the monomers and polymers are presented in Table II.

**Fractionation and Kuhn–Mark–Houwink–Sakurada (KMHS) Relations.** Several samples of each polymer were fractionated as described. The molecular weight distribution of the whole polymers was controlled by application of the relation[15]

$$\bar{M}_w/\bar{M}_n = \sum_{i=1}^{\infty} g_i M_i \sum_{i=1}^{\infty} g_i/M_i \qquad (1)$$

where $g_i$ represents the weight fraction of the *i*th polymer fraction and $M_i$ its molecular weight. Values of the order of 1.7–2.1 were obtained, which are obviously too low, as a consequence of usually discarding head and tail fractions of low molecular weight. A calculation of relation 1 for one sample of PDBzI comprised 17 fractions with $M_i$ values from $31.7 \times 10^3$ to $851 \times 10^3$ and an $\bar{M}_w/\bar{M}_n$ relation of 1.92. Similar values resulted also in other cases.

From $\bar{M}_w$ and $[\eta]$ values of selected fractions the KMHS relations for each polymer, referring to toluene at 25 °C, were calculated by the least-squares method. The relation for PDEFI was obtained from measured values of $\bar{M}_w$ and limiting viscosities presented in Table III, while the true values for PDBzI and PDPFI are presented graphically in Figure 2. The correlation factor for the statistically calculated linear KMHS relation was determined according to

$$w\ (\%) = \left[\left(\sum_{i=1}^{n} \Delta y_i^2\right)\frac{1}{n}\right] \qquad (2)$$

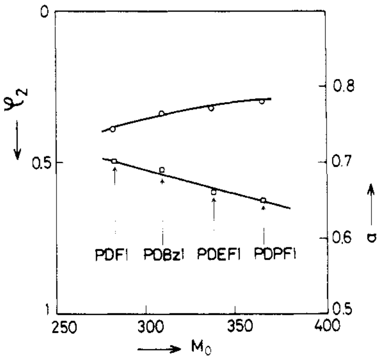


**Figure 1.** Critical volume fractions of methanol $\varphi_2$ (○) in benzene/methanol and the exponent $a$ (□) of the KMHS relation in toluene at 25 °C vs. the molecular weight $M_0$ of the repeat unit.

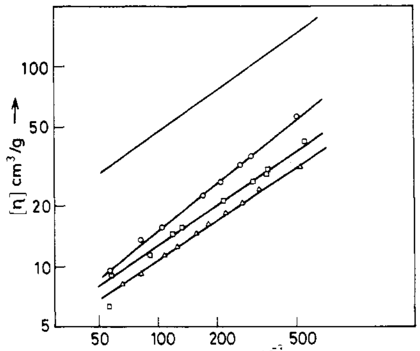


**Figure 2.** Double-logarithmic plots of $[\eta]$ vs. $\bar{M}_w$ for poly(styrene) (—), poly(diethyl itaconate) (○), PDBzI (□), and PDPFI (△) in toluene at 25.0 °C.

with usual notation of the symbols.

All the results defining the KMHS relations and its limitations as well as those of the Huggins constants observed from $[\eta]$ extrapolations are collected in Table IV.

With the increase of the number of methylene groups in the substituents, the KMHS exponent $a$ gradually decreases, indicating a lowering of the long-range interaction in toluene. Figure 1, including also the data for the first member of the series, PDFI,[6] represents graphically this change; the decreasing value of $\varphi_2$, the critical nonsolvent fraction of methanol to produce first turbidities, reflects in a similar way the decreasing solvent power of benzene.

The decrease of the KMHS exponent $a$, when introducing methylene groups into the substituents in the same way, was observed before for two other polymer homologous series: poly(di-*n*-alkyl itaconates)[3] and poly[(bis-

Table IV
Data on KMHS Relations of PDBzI, PDEFI, and PDPFI in Toluene at 25 °C[a]

| polymer | KMHS constant $K \times 10^{-3}$ | KMHS exponent $a$ | Huggins constant | no. of fractions | $\bar{M}_w \times 10^{-3}$ | corr factor, % |
|---|---|---|---|---|---|---|
| PDBzI | 4.47 | 0.69 | 0.36 | 9 | 57-565 | 2.9 |
| PDEFI | 5.26 | 0.66 | 0.40 | 8 | 90-450 | 2.4 |
| PDPFI | 5.97 | 0.65 | 0.45 | 12 | 65-524 | 3.4 |

[a] KMHS relation for PDFI:[6] $[\eta] = 3.6 \times 10^{-3}\bar{M}_w^{0.70}$.

Table V
$K_\Theta$ and $B$ Values for Poly[bis(phenyl-*n*-alkyl) itaconates] according to Various Extrapolation Methods

| | $K_\Theta \times 10^3$, $cm^3\ g^{-3/2}\ mol^{1/2}$ | | | | $B \times 10^{28}$, $cm^3\ g^{-2}\ mol^2$ | | |
|---|---|---|---|---|---|---|---|
| polymer | FFS | FFS corr | KS | SF | FFS | KS | SF |
| PDFI[a] | 20.0 | 28.7 | 28.9 | 28.9 | | 1.6 | 1.4 |
| PDBzI | 20.2 | 28.4 | 28.6 | 28.2 | 3.1 | 2.6 | 2.4 |
| PDEFI | 21.1 | 28.1 | 25.7 | 25.6 | 1.6 | 1.8 | 1.6 |
| PDPFI | 22.7 | 29.7 | 25.6 | 25.2 | 1.5 | 2.0 | 1.7 |

[a] Reference 6.

(cyclohexyl-*n*-alkyl) itaconates].[4] In all these series the introduction of $CH_2$ groups results in a reduction of the contour length of the chain and in a shrinkage of the coil due to diminishing long-range interactions.

$[\eta]$ values are rather low when compared with those of other vinyl monomers of much lower monomer molecular weight. An illustration of this statement is presented in Figure 2, representing the KMHS relations in toluene at 25 °C for poly(styrene),[16] poly(diethyl itaconate),[3] PDBzI, and PDPFI: for any arbitrarily chosen $\bar{M}_w$ ordinate, the corresponding $[\eta]$ drops approximately by 1 order of magnitude when the substituent of the repeat unit changes from a single phenyl to the two long and bulky substituents in the polymers in this investigation.

**Unperturbed Dimensions.** The unperturbed dimensions of the polymers investigated were obtained by extrapolating the viscosity behavior in toluene described in the KMHS relations to Θ-conditions in the way done previously for other poly(itaconates)[4-7] and other polymers described in the literature.[16] In order to obtain $K_\Theta$, extrapolations were performed according to the methods proposed by Flory, Fox, and Schaefgen (FFS)[17]

$$[\eta]^{2/3}/M^{1/3} = K_\Theta^{2/3} + 0.858K_\Theta^{2/3}\phi_0 BM/[\eta] \qquad (3)$$

Kurata and Stockmayer (KS)[17]

$$[\eta]^{2/3}/M^{1/3} = K_\Theta^{2/3} + 0.363B\phi_0 g(\alpha_\eta)M^{2/3}/[\eta]^{1/3} \qquad (4)$$

and Stockmayer and Fixman (SF)[18]

$$[\eta]/M^{1/2} = K_\Theta + 0.51B\phi_0 M^{1/2} \qquad (5)$$

In these relations $K_\Theta$ represents the KMHS constant $K$ at Θ-conditions, $\phi_0$ is the universal Flory constant, equal to $2.7 \times 10^{21}$, as suggested for sharp fractions,[19] $\alpha_\eta$ is the viscosity expansion coefficient, $g(\alpha_\eta) = 8/(3\alpha_\eta + 1)^{3/2}$ in (4) is a function applied iteratively to obtain a more precise intercept, and $B$ is a thermodynamic constant related to the polymer/solvent interaction parameter $\chi$:

$$B = V_2(1 - 2\chi)/V_1 N_A \qquad (6)$$

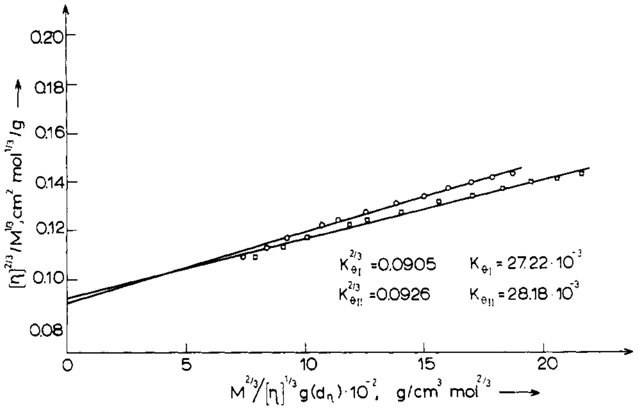


**Figure 3.** Kurata–Stockmayer extrapolation plot for PDBzI: (○) $g(\alpha_\eta) = 1$; (□) corrected with the true value of $g(\alpha_\eta)$.

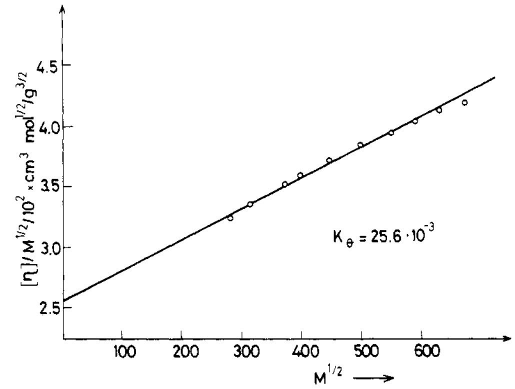


**Figure 4.** Stockmayer–Fixman extrapolation plot for PDEFI.

Extrapolation diagrams according to relations 4 and 5 are presented in Figures 3 and 4. Due to relatively small KMHS exponents, a single adjustment proved sufficient for relation 4.

The values for $K_\Theta$ and for $B$ for the three polymers, as well as those for PDFI,[6] are assembled in Table V. Good agreement for $K_\Theta$ obtained according to the methods of KS and SF is observed, as well as a decreasing tendency in going from lower to higher members of the polymer series. $K_\Theta$ according to FFS are, however, much lower. The disagreement can be minimized by dividing $K_\Theta$ from the FFS plot by

$$\phi(\epsilon)/\phi_0 = (1 - 2.63\epsilon + 2.83\epsilon^2) \qquad (7)$$

according to Ptitsyn and Eisner,[20] noting the difference between the viscosity and thermodynamic expansion factors $\alpha_\eta$ and $\alpha$, disregarded in (3). In this relation, $\epsilon$ equals $2/3(1 + a) - 1$, where $a$ is the KMHS exponent. In this way better agreement for $K_\Theta$ is obtained, at least for

Table VI
σ-Values for Poly(itaconates) with Different R Substituents[a]

| | R = $(CH_2)_nC_6H_5$ | | | R = $(CH_2)_nC_6H_{11}$ | | R = $(CH_2)C_6H_{13}$ | |
|---|---|---|---|---|---|---|---|
| *n* | polymer | σ ($\sigma_{FFS}$) | $C_\infty$ | polymer | σ | polymer | σ |
| 0 | PDFI<br>($M_0$ = 282) | 2.60 (2.60) | 13.4 | PDCHI<br>($M_0$ = 294) | 2.99 | PDHI<br>($M_0$ = 296) | 2.90 |
| 1 | PDBzI<br>($M_0$ = 310) | 2.69 (2.69) | 14.6 | PDMCHI<br>($M_0$ = 322) | 2.75 | PDHpI<br>($M_0$ = 324) | 3.00[b] |
| 2 | PDEFI<br>($M_0$ = 338) | 2.72 (2.78) | 14.8 | PDECHI<br>($M_0$ = 350) | 2.83 | PDOI<br>($M_0$ = 352) | 3.09 |
| 3 | PDPFI<br>($M_0$ = 366) | 2.81 (2.91) | 15.6 | PDPCHI<br>($M_0$ = 378) | 2.89 | PDNI<br>($M_0$ = 380) | 3.20[b] |

[a] Abbreviations: PDCHI = poly(dicyclohexyl itaconate), PDMCHI = poly[bis(cyclohexylmethyl) itaconate], PDECHI = poly[bis(cyclohexylethyl) itaconate], PDPCHI = poly[bis(cyclohexyl-*n*-propyl) itaconate], PDHI = poly(di-*n*-hexyl itaconate), PDHpI = poly(di-*n*-heptyl itaconate), PDOI = poly(di-*n*-octyl itaconate), PDNI = poly(di-*n*-nonyl itaconate).
[b] From interpolations.

PDBzI, as shown for corrected FFS values in Table V. The lower $B$ values for PDEFI and PDPFI relative to PDBzI are in agreement with the better solvent power of toluene.

Values of $K_\Theta$ obtained according to the method KS were taken to calculate the unperturbed dimensions, since previous reports on poly(itaconate) unperturbed dimensions[4-7] are based on this extrapolation procedure and also since the KS relation, although partly empirical, may be considered as an improvement of similar relations published previously in the literature.[17] $K_\Theta$ was introduced into the Flory–Fox relation

$$K_\Theta = \phi_0(r_0^2/M)^{3/2} \quad (8)$$

where $\bar{r}_0^2$ is the mean end-to-end distance in the unperturbed state. Comparing the right-hand side of expression 8 with $\bar{r}_{0f}^2/M$, referring to a freely rotating chain, the $\sigma$-parameter, which is a measure of hindrance of free rotation of carbon atoms of the main chain, was obtained from the relation

$$\sigma = (\bar{r}_0^2)^{1/2}/(\bar{r}_{0f}^2)^{1/2} \quad (9)$$

Alternatively, to obtain the unperturbed state, the characteristic ratio[19] $C_\infty$, claimed to be a better criterion for this polymer property, was obtained from the relation

$$C_\infty = (K_\Theta/\phi_0)^{3/2} m/l^2 \quad (10)$$

where $l$ is the length of the carbon-to-carbon valence bond and $m$ is the average molecular weight per unit skeletal link of the backbone chain. Both values expressing the polymer unperturbed states are presented in Table VI. The table also contains values of $\sigma$ resulting from the FFS $K_\Theta$ values and $\sigma$-values for poly($n$-alkyl itaconates)[3] and poly(cyclohexylalkyl itaconates)[4] of comparable repeat unit molecular weights ($M_0$) in order to discuss the effect of the substituent configuration on $\sigma$.

From the results presented in Table VI various conclusions can be drawn. Regarding the $\sigma$-values obtained from $K_\Theta$ according to the methods of KS and FFS, differences are observed only for the last two members of the series. The values according to the latter extrapolation in this case seem, however, to be overestimated, as it is improbable that they would reach the level of corresponding poly(itaconates) with bulky cyclohexyl groups attached at the end of the R substituents.

For the series investigated in this work, both $\sigma$ and $C_\infty$ increase slowly and monotonously. This effect results from the increase of the size of the substituent as a whole, although by introduction of methylene(s) free rotation in both substituents around the carbon-to-carbon bonds connecting $-COO-$ and $-CH_2-$ and $-CH_2-$ and phenyl is gained. This rotation is restricted in PDFI due to hyperconjugation and dipole–dipole interaction.[21] The absolute values of $\sigma$ and especially of $C_\infty$ are significantly above such values reported for most vinyl polymers.[16] In this respect the size of the substituents seems to be of predominant importance, with the presence of two substituents per repeat unit being of minor influence: the $\sigma$-value of poly(dimethyl itaconate)[3] is only 2.02 units. It is assumed that the high hindrance to rotation is of importance in the polymerization process, resulting in low rates and promoting chain-transfer reactions, as observed in preparation of the polymers for this investigation.

Comparison of the first and the second polymer homologous series from Table VI reveals that, the more voluminous cyclohexyl causes greater short-range interaction than the smaller planar stiff phenyl ring. This effect, however, vanishes slowly when the ring is distanced stepwise more and more from the polymer backbone. Thus when phenyl and cyclohexyl are attached through a trimethylene chain, close $\sigma$-values are obtained. Any correlation with poly(di-$n$-alkyl itaconates) from the last column in the table is less evident. In this series $\sigma$ rises constantly with increasing $n$.[22] The hindrance to rotation is higher for any polymer of the two other series with an approximately equal repeat unit molecular weight, although it might be expected that the numerous possible conformations of $n$-alkyl groups in the substituents would not contribute very much to the hindrance of rotation.

**Acknowledgment.** We express our thanks to the Scientific Fund of the Socialist Republic of Serbia for financial support.

**Registry No.** PDBzI, 58991-68-7; PDEFI, 73345-35-4; PDPFI, 73345-37-6; PDFI, 58991-66-5.

## References and Notes

(1) Kobayashi, T. *Process Biochem.* **1978**, *13* (May).
(2) Tate, B. E. *Fortschr. Hochpolym. Forsch.* **1967**, *5*, 214.
(3) Veličković, J.; Vasović, S. *Makromol. Chem.* **1972**, *153*, 207.
(4) Veličković, J.; Filipović, J.; Čoseva, S. *Eur. Polym. J.* **1979**, *15*, 521.
(5) Veličković, J.; Filipović, J. *Angew. Makromol. Chem.* **1977**, *57*, 139.
(6) Veličković, J.; Plavšić, M. *Eur. Polym. J.* **1975**, *11*, 377.
(7) Veličković, J.; Filipović, J. *Polym. Bull.* **1981**, *5*, 569.
(8) Cowie, J. M. G.; McEwen, I. J.; Veličković, J. *Polymer* **1975**, *16*, 869.
(9) Cowie, J. M. G.; Henschall, S. A. E.; McEwen, I. J.; Veličković, J. *Polymer* **1977**, *18*, 613.
(10) Cowie, J. M. G.; Haq, Z.; McEwen, I. J.; Veličković, J. *Polymer* **1981**, *22*, 327.
(11) Askarov, M. A.; Gafurov, B. L. "Syntez i Polymerizacija Itakonatov"; FAN, Ed.; Taschkent, USSR, 1979.
(12) Veličković, J.; Petrović-Djakov, D.; Filipović, J. *Angew. Makromol. Chem.* **1983**, *113*, 21.
(13) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1093.
(14) Hummel/Scholl, "Atlas der Polymer- und Kunststoffanalyse"; C. Hanser Verlag: München, Wien, 1978; Vol. 1, p 292.
(15) Tung, L. H. In "Polymer Fractionation"; Cantow, M. J., Ed.; Academic Press: New York, 1967; p 368.
(16) Kurata, M.; Tsunashima, Y.; Imawa, M.; Kamada, K. In "Polymer Handbook"; Brandrup, J., Immergut, E., Eds.; Interscience: New York, 1974; Chapter IV, pp 1–18.
(17) Kurata, M.; Stockmayer, W. *Fortschr. Hochpolym. Forsch.* **1963**, *3*, 196.
(18) Stockmayer, W.; Fixman, M. *J. Polym. Sci., Part C* **1963**, *1*, 137.
(19) Flory, P. J. In "Statistical Mechanics of Chain Molecules"; Interscience: New York, London, 1969; pp 35–42.
(20) Ptitsyn, O.; Eisner, U. *Zh. Fiz. Khim.* **1958**, *32*, 2464.
(21) Hummel, J. P.; Flory, P. J. *Macromolecules* **1980**, *13*, 479.
(22) Veličković, J.; Filipović, J. *Makromol. Chem.*, in press.