

STUDIES ON POLYMERIZATION KINETICS OF METHYL METHACRYLATE AT HIGH CONVERSION*

LI Bogeng (李伯耿), YU Zaizhang (于在璋), CAI Qizen (蔡启振) and LI Baofang (李宝芳)

(Department of Chemical Engineering, Zhejiang University, Hangzhou)

ABSTRACT

The bulk polymerization of methyl methacrylate which was carried out in a metallic dilatometer and in a differential scanning calorimeter has been studied over the complete course of the reaction. An attempt was made to quantitatively express the relation on the onset of gel effect and the final conversion with polymerization conditions such as temperature, kinds and concentration of initiators. It was demonstrated further that the final conversion of polymerization in homogeneous ideal systems is only dependent upon the reaction temperature.

The polymerization kinetics of methyl methacrylate (MMA) has been studied by many investigators, but most of them were limited to the use of low activity catalyst and the study of the gel effect in various views. The qualitative relation between the onset conversion of gel effect as well as the critical conversion of autoacceleration and polymerization conditions had been discussed by the present authors^[1], and three methods to determine the critical conversion were reviewed. This paper is further concerned with the kinetics of methyl methacrylate at high conversion in a metallic dilatometer and in a differential scanning calorimeter (DSC). An attempt was made to express the quantitative relations on the onset of gel effect and the final conversion with reaction conditions.

EXPERIMENTAL

1. Materials

Methyl methacrylate was of polymerization reagent quality, and further purified by distillation. Initiator (DCPD) was purified by soaking it in methanol, followed by drying in vacuum, and its purity was analysed by iodimetry. All solvents and precipitant such as acetone, chloroform and methanol were of analytical reagent quality.

2. Apparatus and procedure

Polymerizations were carried out in a metallic dilatometer as shown in Fig. 1. The polyester film pocket containing monomer and initiator was double-layered between two separate metallic shells. Water was poured into the dilatometer through a needle valve and air was removed through the exhaust cock. The dilatometer was then immersed in the thermostated water-bath (within $\pm 0.05^\circ\text{C}$). The extent of reaction was estimated from the

* Received August 19, 1983

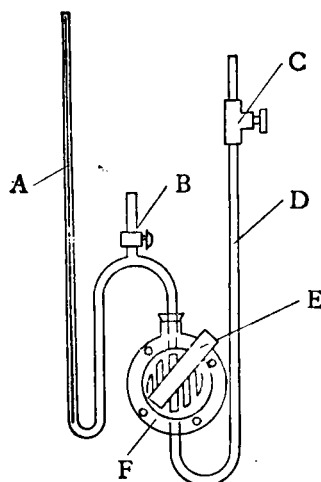


Fig. 1 Schematic diagram of metallic dilatometer
(A) Glass capillary tube, (B) Exhaust cock, (C) Needle valve,
(D) Stainless steel tube, (E) Polyester film pocket, (F) Brass shell.

contraction of the mercury level in the capillary tube of the dilatometer.

The formula for calculating the reaction conversion given in literature^[2] is as follows:

$$x (\%) = \frac{H_0 - H_t}{H_0 - H_f} x_f \times 100\% \quad (1)$$

where H_0 , H_f and H_t are the mercury levels in the capillary tube at the time of the beginning, stopping of the contraction and t , respectively, and x_f is the final conversion obtained by other methods such as precipitation and DSC.

It was considered by the present authors that there is an unisothermal polymerization stage after the dilatometer is immersed in the thermostated water-bath, the conversion of which is not too small to be neglected, and Eq. (1) should be modified as follows

$$x (\%) = \left[\frac{H_0 - H_t}{H_0 - H_f} (x_f - x_0) + x_0 \right] \times 100\% \quad (2)$$

where x_0 is the conversion during temperature rising, which was calculated by the stationary state kinetic equation of free-radical polymerization as well as the mean temperature and the temperature-rising time.

After polymerization was completed, the product was taken out from the film pocket, weighed, dissolved in a mixture of acetone and chloroform, and then precipitated twice in methanol, so the final conversion was determined. The pure polymer obtained by precipitation was used to measure the molecular weight by means of viscosimetry.

The polymerization course was also investigated with a Model CDR-1 DSC. After isothermal polymerization, the sample was heated at constant heating rate so that the residual monomer was fully polymerized. The final conversion in an isothermal polymerization was calculated as a fraction of the exothermic energy at the isothermal run to the sum of the energies at the isothermal and rising temperature runs^[3, 4].

RESULTS AND DISCUSSION

The relations between the reaction time and the conversion for DCPD-MMA system either at 50°C and various concentrations of initiator or at the concentration of initiator $[I]=5\times 10^{-3}$ mol/l and various temperatures, were investigated in a metallic dilatometer. The results were illustrated in Figs. 2 and 3. These were converted into the relation between the polymerization rate and the conversion as shown in Figs. 4 and 5.

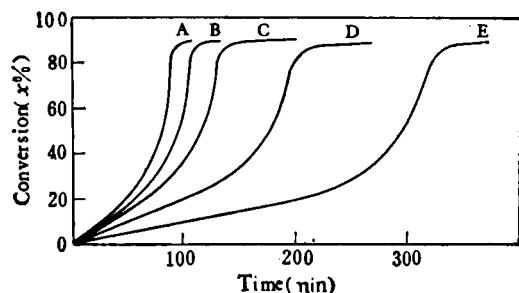


Fig. 2 Plots of conversion vs. time at $T=50^{\circ}\text{C}$ and various initiator concentrations: $[\text{DCPD}]\times 10^3$ (mol/l)=(A) 11, (B) 8, (C) 5, (D) 2, (E) 0.9.

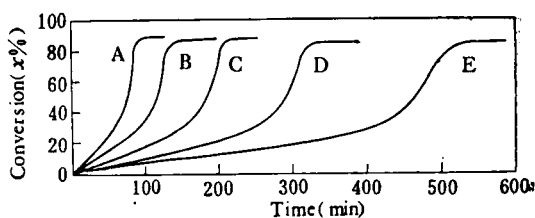


Fig. 3 Plots of conversion vs. time at $[\text{DCPD}]=5\times 10^{-3}$ (mol/l) and various polymerization temperatures: (A) 55°C , (B) 50°C , (C) 45°C , (D) 40°C , (E) 35°C .

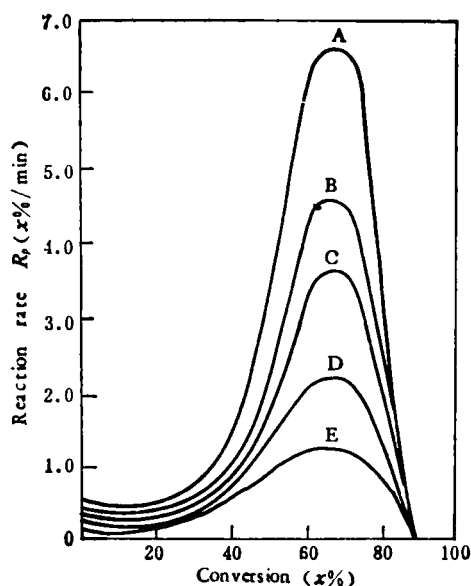


Fig. 4 Plots of reaction rate vs. conversion at $T=50^{\circ}\text{C}$ and various initiator concentrations: $[\text{DCPD}]\times 10^3$ (mol/l) = (A) 11, (B) 8, (C) 5, (D) 2, (E) 0.9.

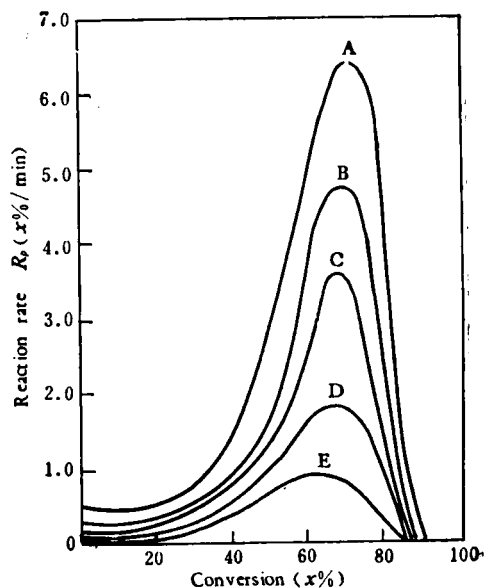


Fig. 5 Plots of reaction rate vs. conversion at $[\text{DCPD}]=5\times 10^{-3}$ (mol/l) and various polymerization temperatures: (A) 55°C , (B) 50°C , (C) 45°C , (D) 40°C , (E) 35°C .

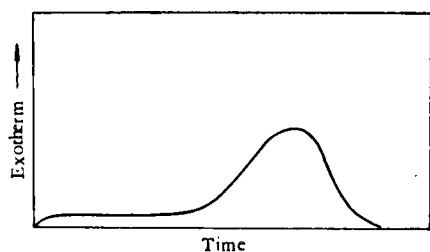


Fig. 6 DSC thermogram of isothermal bulk polymerization of MMA

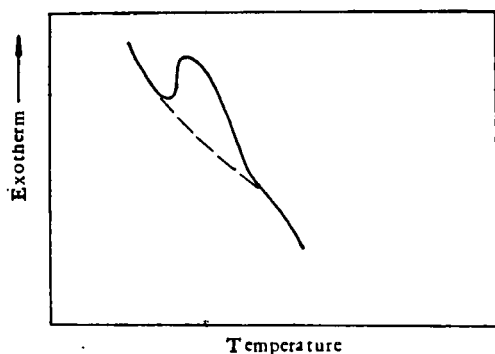


Fig. 7 DSC thermogram at rising temperature scanning of PMMA polymerized isothermally

At the same condition, isothermal polymerization was carried out in a DSC, followed by rising temperature scanning. The typical thermograms were shown in Figs. 6 and 7.

1. *Determination of the gel effect onset and discussion about the quantitative relation between the critical conversion and the reaction conditions*

It has been considered by Burnett et al.^[5] that for MMA polymerization, the onset of the gel effect depends on the collection of radicals in the reaction system. They supposed the rate of increase in the number of radical to be proportional to the concentration of polymer formed, and assumed the monomer concentration to be constant in the vicinity of the radicals, so the following equation was derived

$$\left(\frac{R_x}{R_0} - 1\right)^{1/2} = K_1^{1/2}(x - x_1) \quad (3)$$

where R_0 and R_x are rates of polymerization at conversion 0 and x , respectively; $K_1 = \frac{1}{2}k_1(k_i/R_i)^{1/2}$, k_1 is a constant, and R_i is the initiation rate. Equation (3) requires that the plot of $(R_x/R_0 - 1)^{1/2}$ against x over the accelerated stage of reaction should be linear, with intercept on the conversion axis equal to x_1 —the conversion at which the “autoacceleration effect” begins, i. e., $R_x = R_0$.

O'Driscoll et al.^[6] have given a precise definition for the critical conversion of gel effect recently. For bulk polymerization, there must be a minimum of the reaction rate in the plot of rate of polymerization against percent conversion, and it would be more obvious for the system of high temperature or high active initiator. O'Driscoll defined the conversion corresponding to the minimum of rate as the critical conversion of the gel effect x_g . It is difficult to accurately find the minimum by the visual method, because the points of experimental data are scattered in the figure of rate against conversion, so O'Driscoll suggested that a polynomial should be determined by the method of least-squares from a certain set of discrete points, and then x_g could be calculated by the extreme value of the polynomial. It is obvious that O'Driscoll's definition is exact, but calculating x_g is complex.

With regard to Eq. (3), we considered that the concentration of monomer must be largely changed in the moderate conversion, and it cannot be regarded as a constant, so

Eq. (3) should be modified into the following equation to get the critical conversion of gel effect x_1'

$$\left[\frac{R_x}{R_0(1-x)} - 1 \right] = K_1^{1/2} (x - x_1') \quad (4)$$

By plotting the left hand side of Eq. (4) against x , a straight line is obtained, the value of x_1' given by the intersection of that and the x axis are recorded in Tables 1 and 2. x_1 given by Burnett's method and x_g given by O'Driscoll's visual method are recorded altogether for comparison. It is seen that x_1 given by Burnett's method is always larger than x_g , but x_1' given by the modified Burnett's method is close to x_g , and the modified Burnett's method is simpler than O'Driscoll's.

Table 1 Critical conversion of gel effect (or autoacceleration) at various initiator concentrations (50°C)

$[I] \times 10^3$ (mol/l)	Methods		
	O'Driscoll's x_g	Burnett's x_1	Modified Burnett's x_1'
11	0.17	0.1982	0.1901
8	0.14	0.2190	0.1661
5	0.13	0.1812	0.1484
2	0.12	0.1917	0.1236
0.9	0.08	0.1074	0.0962

Table 2 Critical conversion of gel effect (or autoacceleration) at various polymerization temperature ($[I] = 5 \times 10^{-3}$ mol/l)

T (°C)	Methods		
	O'Driscoll's x_g	Burnett's x_1	Modified Burnett's x_1'
55	0.19	0.2250	0.1752
50	0.13	0.1812	0.1484
45	0.12	0.1736	0.1293
40	0.12	0.1449	0.1131
35	0.13	0.1557	0.1260

x_g is increased with an increase in the concentration of initiator or the polymerization temperature, it indicates that as the molecular weight and system viscosity decrease, x_g must be enlarged to engender the gel effect.

So far, there is almost no paper concerning the quantitative relation between the critical conversion of gel effect and polymerization conditions. Turner and Lee^[7] have proposed the following empirical formula expressing the relation between the critical polymerization degree of the gel effect $\bar{X}_{nc}$ and the volume fraction of polymer ϕ_p in the polymerization system

$$\bar{X}_{nc}^\alpha \cdot \phi_p = K \quad (5)$$

where K and α are characteristic constants for the polymerization system. For PMMA-MMA system, it has been given by Lachinow et al.^[8] through experimental measurement that $K=0.74$, and $\alpha=0.53$.

In respect that the polymerization course follows the principle of stationary state before gel effect, now we introduce the definition of the kinetic chain length at low conversion

$$\nu = \frac{k_p}{(2fk_d k_t)^{1/2}} \cdot \frac{[M]}{[I]^{1/2}} \quad (6)$$

When the effect of the concentration factor $\frac{[M]}{[I]^{1/2}}$ on ν is neglected, the average polymerization degree is given by

$$\bar{X}_{nc} = \frac{\nu_0}{\frac{c}{2} + D} = \frac{1}{\frac{c}{2} + D} \cdot \frac{k_p}{(2fk_d k_t)^{1/2}} \cdot \frac{[M]_0}{[I]_0^{1/2}} \quad (7)$$

Assuming that the initiator efficiency f , the fractions of coupling termination C and disproportionating termination D are all constants over the range of a small change in temperature, and then the following equation is derived from Eqs. (6) and (7):

$$\bar{X}_{nc} = k' \frac{k_p}{(k_d k_t)^{1/2}} \cdot \frac{[M]_0}{[I]_0^{1/2}} \quad (8)$$

where the constant $k' = \frac{1}{\frac{c}{2} + D} \cdot \frac{1}{(2f)^{1/2}}$.

Substituting Eq. (8) into Eq. (5), leads to

$$\phi_p = K' \left[\frac{k_p}{(k_d k_t)^{1/2}} \cdot \frac{[M]_0}{[I]_0^{1/2}} \right]^{-\alpha} \quad (9)$$

$$\ln \phi_p = \ln K' - \alpha \ln \left[\frac{k_p}{(k_d k_t)^{1/2}} \cdot \frac{[M]_0}{[I]_0^{1/2}} \right] \quad (10)$$

where

$$K' = \left[(2f)^{1/2} \left(\frac{c}{2} + D \right) \right]^\alpha \cdot K$$

The relation between the volume fraction ϕ_p and conversion x in the system can be written as

$$\phi_p = \frac{1}{1 + \left(\frac{1}{x} - 1 \right) \frac{\rho_p}{\rho_m}} \quad (11)$$

or

$$x = \frac{1}{1 + \left(\frac{1}{\phi_p} - 1 \right) \frac{\rho_m}{\rho_p}} \quad (12)$$

where ρ is the density and the subscripts p and m represent polymer and monomer, respectively. With respect of the DCPD-MMA system, substituting x_1' given by modified Burnett's method into Eq. (11) to get ϕ_p and then plotting $\ln \phi_p$ against

$\ln \left[\frac{k_p}{(k_d k_t)^{1/2}} \cdot \frac{[M]_0}{[I]_0^{1/2}} \right]$, a good straight line is obtained as shown in Fig. 8, it gives $\alpha=0.5353$, $K'=6.583$ with intercept and slope, so Eq. (9) may be rewritten as

$$\phi_p = \frac{1}{1 + \left(\frac{1}{x} - 1 \right) \frac{\rho_p}{\rho_m}} = 6.583 \left[\frac{k_p}{(k_d k_t)^{1/2}} \cdot \frac{[M]_0}{[I]_0^{1/2}} \right]^{-0.5353} \quad (13)$$

It is obvious that when $[M]_0$, $[I]_0$ and other parameters such as k_d , k_p and k_t at reaction temperature are known, the critical conversion of gel effect x_g corresponding to this polymerization condition can be obtained.

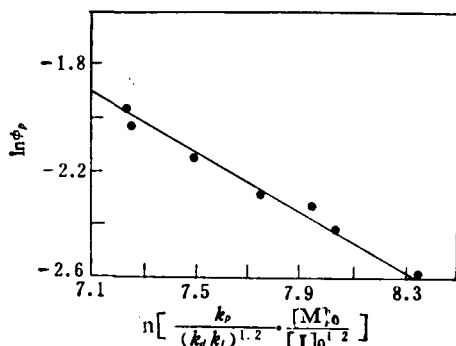


Fig. 8 $\ln \phi_p$ vs. $\ln \left[\frac{k_p}{(k_d k_t)^{1/2}} \cdot \frac{[M]_0}{[I]_0^{1/2}} \right]$

x_g in various reaction conditions given by Eq. (13) are shown in Table 3, and are compared with the x'_1 given by modified Burnett's equation (4), where k_d , k_p and k_t are calculated by using the data in literature [9], and k_d of DCPD in literature [10].

Table 3 Comparison of x_g calculated by Eq. (13) with x'_1 given by Eq. (4) in various polymerization conditions

T ($^{\circ}\text{C}$)	Kinds of initiator	$[I] \times 10^3$ (mol/l)	x'_1 (%)	x_g (%)
55 50 45 40 35	DCPD	5	17.53	17.34
			14.84	15.13
			12.93	13.13
			11.31	11.33
			12.60	9.73
50	DCPD	11	19.01	18.54
		8	16.61	17.08
		2	12.36	11.93
		0.9	9.62	9.68
50	BPO	11	6.80	5.66
50	AIBN	11	8.90	9.21

It is seen from Table 3 that the critical conversion of gel effect calculated by the newly proposed equation is in good agreement with experimental data. It indicates that Eq. (13),

is suitable for the bulk polymerization of MMA in various conditions. An enlightenment was gained from above discussion, which a similar quantitative relation can certainly be obtained for other homogeneous polymerization systems.

2. Determination of the final conversion and discussion about the quantitative relation between that and the reaction conditions

Burnett^[4] and Schulz^[11] have found that the relation between the final conversion and polymerization temperature is approximately linear, but they did not give a substantive explanation and quantitative treatment.

Kelly and Bueche^[12] have derived the glass transition temperature of a polymer-monomer mixture T_g as the following equation on the basis of the free volume theory

$$T_g = \frac{\alpha_p \phi_p T_{gp} + \alpha_m (1 - \phi_p) T_{gm}}{\alpha_p \phi_p + \alpha_m (1 - \phi_p)} \quad (14)$$

where ϕ is the volume fraction in the system, α is the volume expansion coefficient, T_g is the glass transition temperature and the subscripts p and m represent polymer and monomer, respectively.

According to Fox and Flory, the glass transition temperature of polymer (T_{gp}) is a function of its molecular weight as follows^[13]:

$$T_{gp} = T_{g\infty} - K/\bar{M}_n \quad (15)$$

where $T_{g\infty}$ is the glass transition temperature of polymer with infinite molecular weight and K is a constant, for PMMA $T_{g\infty} = 114^\circ\text{C}$ ^[4], and $K = 2 \times 10^5$ ^[14].

In discussing Kelly-Bueche equation, Horic^[4] suggested that for the polymer-monomer system, the glass transition temperature T_g should be equal to the polymerization temperature, otherwise polymerization runs on because the system is in viscous liquid state. On giving α_m , α_p , T_{gp} , T_{gm} and polymerization temperature T_p , the final volume fraction of polymer or the final conversion of polymerization could be calculated by Eqs. (14) and (12).

For polymerization of MMA, setting $\alpha_m = 1.3 \times 10^{-3}/^\circ\text{C}$, $\alpha_p = 4.9 \times 10^{-4}/^\circ\text{C}$ and $T_{gm} = -106^\circ\text{C}$ ^[4], the final conversion x_f values listed in Tables 4 and 5 were obtained by substituting $\bar{M}_n$ values measured in various reaction conditions into Eq. (15) and using Eqs. (14) and (12). x_f measured by precipitation analysis and by DSC were also listed. It has been found that the final conversion given by these three methods are quite close. DSC method is very simple, however calculating by Kelly-Bueche's equation can show a small difference in x_f values.

It was also seen that the final conversion of polymerization is only a function of reaction temperature, and independent of the concentration of initiator in the range of the present investigation. This can be explained that T_{gp} is nearly constant i. e., $\bar{M}_n$ almost has no any effect on the glass transition temperature of polymer (as shown in Tables 4 and 5) when the molecular weights which exceed a limiting value are substituted into Fox-Flory equation, although the molecular weights vary largely at different conditions of polymerization. Thus it is concluded that the final conversion of polymerization in homogeneous ideal system is only dependent on reaction temperature and nearly has no relation with initiator activity and its concentration.

Table 4 Final conversion of MMA at various initiator concentrations (50°C)

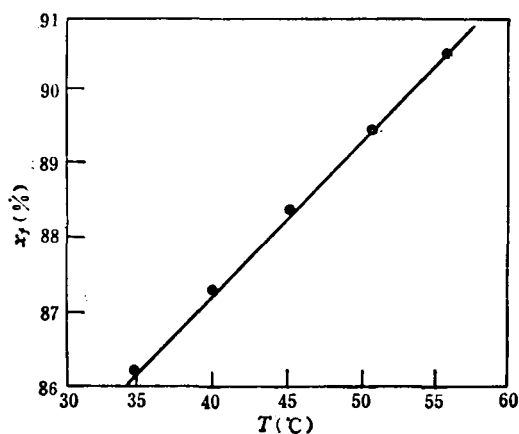
$[I] \times 10^3$ (mol/l)	$\overline{M}_n \times 10^{-6}$	T_{gp} (°C)	ϕ_p (%)	Final conversion x_f (%)		
				Kelly's Eq.	Precipitation	DSC
11	0.703	113.69	86.66	89.56	88.95	88.83
8	0.792	113.72	86.66	89.55	88.54	87.54
5	1.134	113.81	86.64	89.54	90.37	89.88
2	1.675	113.87	86.63	89.53	90.16	88.80
0.9	2.369	113.91	86.62	89.53	89.16	

Table 5 Final conversion of MMA at various polymerization temperatures ($[I]=5 \times 10^{-3}$ mol/l)

T (°C)	$\overline{M}_n \times 10^{-6}$	T_{gp} (°C)	ϕ_p (%)	Final conversion x_f (%)	
				Kelly's Eq.	Precipitation
55	0.903	113.76	87.9	90.58	92.41
50	1.134	113.81	86.6	89.54	90.37
45	1.426	113.85	85.3	88.42	87.72
40	1.859	113.88	84.0	87.32	86.93
35	2.367	113.91	81.2	86.05	86.23

By plotting x_f (calculated by Kelly-Bueche equation) against reaction temperature t (°C), a straight line was obtained as shown in Fig. 9. The following empirical formula which represents the relation between the final conversion and polymerization temperature is given by regress treatment

$$x_f (\%) = 0.225 t (\text{°C}) + 78.25 \quad (16)$$

**Fig. 9** Plot of the final conversion x_f vs. polymerization temperature

So long as the molecular weight exceeds a limiting value (about 200,000), the final conversion in various reaction temperatures can be calculated by Eq. (16).

Acknowledgement The authors are grateful to Miss Cai Cichun, Mr. Gu Chenghe and Mr. Hou Jingping for their participation in part of this work, and to Professor Pan Zuren for enthusiastic guidance.

REFERENCES

- [1] 于在璋、李宝芳, 塑料工业, **1980**, *5*, 1.
- [2] 蔡明志、王佩章、卢英敏、王洪山、陈冠华、王玉梅, 合成橡胶工业, **1981**, *5*, 384.
- [3] Malavasic T., Vizovisek, I., Laparje, S. and Moze, A., *Makromol. Chem.*, **1974**, *175*, 873.
- [4] Horic, K., Mita, I. and Kambe, H., *J. Polymer Sci. A-1*, **1968**, *6*, 2663.
- [5] Burnett, G. M. and Duncan, G. L., *Makromol. Chem.*, **1962**, *51*, 154.
- [6] Dionisio, J., Mahabahi, H. K. and O'Driscoll, K. F., *J. Polymer Sci., Polym. Chem. Ed.*, **1979**, *17*, 7.
- [7] Lee, H. B. and Turner, D. T., *Macromolecules*, **1977**, *10* (231), 266.
- [8] Lachinow, M. B., Simonian, R. A., Georgieva, T. G., Zubov, V. P. and Kabanov, V. A., *J. Polymer Sci., Polym. Chem. Ed.*, **1979**, *17*, 613.
- [9] Brandrup, J. and Immergut, E. H., *Polymer Handbook*, 2nd, Wiley-Interscience, New York, **1974**.
- [10] 蔡启振、于在璋、李宝芳、潘祖仁, 合成橡胶工业, **1982**, *1*, 36.
- [11] Schulz, G. V., *Z. Physik. Chem.*, NF3, **1956**, 290.
- [12] Kelly, F. N. and Bueche, F., *J. Polymer Sci.*, **1961**, *50*, 549.
- [13] Fox, T. G. and Flory, P. J., *J. Appl. Phys.*, **1950**, *21*, 581; Fox, T. G. and Loshaek, S., *J. Polymer Sci.*, **1955**, *15*, 371.
- [14] Beevers, R. B. and White, E. F. T., *Trans. Faraday Soc.*, **1960**, *56*, 744.