Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Roussel, R. , Galin, M. and Galin, J. C.(1976) 'Free-Radical Copolymerization of Methyl Methacrylate and α-Methacrylophenone. I. Reactivity Ratios', Journal of Macromolecular Science, Part A, 10: 8, 1485 — 1512
To link to this Article: DOI: 10.1080/00222337608060767
URL: http://dx.doi.org/10.1080/00222337608060767

J. MACROMOL. SCI.–CHEM., A10(8), pp. 1485-1512 (1976)

Free-Radical Copolymerization of Methyl Methacrylate and α-Methacrylophenone. I. Reactivity Ratios

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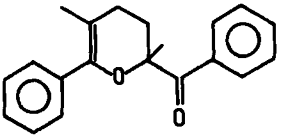
ABSTRACT

The free-radical copolymerization of methyl methacrylate and methacrylophenone (MAP) initiated by azobisisobutyronitrile at 60° C has been studied in ethylbenzene solution and in bulk. The process is characterized by a competitive Diels-Alder condensation of methacrylophenone and by a very low reactivity of methacrylophenone-terminated macroradicals in propagation reactions. The experimental composition data are consistent with a terminal unit model: $\underline{r}_A = 1.77 \pm 0.02$, $\underline{r}_B = 0.110 \pm 0.006$. Copolymerization with depropagation of methacrylophenone-terminated growing chains and copolymerization affected by penultimate effects have been tested as optimized possible models to take into account the inability of MAP to undergo homopolymerization.

INTRODUCTION

During the last five years, copolymers of methyl methacrylate (MMA) and various ketonic monomers have received increased interest as models for fundamental studies of photodegradation processes in polymers, as well as models for new photodegradable materials of technological importance. Copolymers of MMA with methyl vinyl ketone [1-3] and phenyl vinyl ketone [2-4] have been extensively studied, for instance, but α-methacrylophenone [MAP, $CH_2{=}C(CH_3){-}CO{-}C_6H_5$] copolymers seem to have been neglected in spite of their obvious potential interest. To our knowledge, there is only one report in the literature [5] dealing with the polymerization and the copolymerization of MAP. According to Mulvaney et al. [6], MAP is unable to undergo free-radical polymerization. A large range of initiation conditions was investigated between -50 and 100°C, but the only well-characterized product obtained in such reactions was the Diels-Alder cyclic dimer of MAP, 2,5-dimethyl-6 phenyl-2 benzoyl-3,4-dihydro-2 [H] pyran (DA). However, free-radical bulk copolymerization of styrene and MAP, involving probably some penultimate effects, leads to the expected copolymers.



DA

The purpose of the present work is to describe some experimental results related to free-radical MMA–MAP copolymerization with special emphasis on the determination of the reactivity ratios.

EXPERIMENTAL

Reagents and Model Compounds

MAP (monomer B), prepared according to a literature procedure [7], and MMA (monomer A) were twice vacuum-distilled over CaH_2 just before polymerization.

Ethylbenzene and toluene (solvent S) were distilled on a Cadiot spinning-band column.

Azobisisobutyronitrile (AIBN) was twice crystallized from toluene–methanol solution.

DA and polymethacrylophenone (PMAP) were prepared from MAP according to the literature methods [6] by thermal cyclization and by anionic polymerization respectively; $[nBuLi]/[MAP]_0 = 0.03$. After 18 hr at -40° C, the yield of polymeric material is 65%, $\bar{M}_w = 8.5 \times 10^3$ ($dn/dc = 0.216$ ml/g at 25° C in methyl ethyl ketone for $\lambda = 5460$ Å).

Free-Radical Copolymerization

Copolymerizations were carried out at a constant temperature of 60 ± 0.1° C in an all-Pyrex glass reactor protected from light by aluminum foil under a slight pressure of purified argon (≃ 30 Torr), after degassing the reaction medium by three freeze-thaw cycles. The kinetics of the polymerization have been studied by monitoring the decrease of monomer concentration with time by using vapor-phase chromatography. The experimental conditions of chromatographic separation and analysis were the following: Perkin-Elmer 900 chromatograph fitted with flame ionization detector and coupled with an Hewlett-Packard 3370 B electronic integrator; columns (2 m length, 1/8 in. diameter) packed with 5% Silicone SE 30 on Chromosorb G; injector and column temperatures, 200 and 150° C, respectively; nitrogen flow rate, 30 ml/min. In all cases the solvent (ethylbenzene or toluene) was used as internal standard, and the MMA, MAP, and DA concentrations were calculated according to previous calibration with pure compounds.

The copolymers were recovered by precipitation in methanol and dried under vacuum at 50° C. In all cases they were stored and handled in glass vessels protected from light by aluminum foils in order to avoid any photodegradation.

Copolymer Characterization

Composition

The composition of the different samples was systematically determined by elemental analysis, UV and ^{1}H-NMR spectroscopy, and in some cases by additional IR spectroscopy and flash pyrolysis-gas chromatography.

UV spectroscopy was carried out on a Beckman Acta V spectrophotometer. The spectra in dioxane solution were analyzed for PMAP content at λ = 243 nm (phenyl ring $\pi \rightarrow \pi^*$ transition), by using the value of the molar absorptivity measured for anionic PMAP, ϵ = 7830 liter/mole-cm.

IR spectroscopy was performed on a Perkin-Elmer 225 spectrophotometer. The spectra obtained in chloroform solution were analyzed for PMMA and PMAP absorptions at 1728 cm^{-1} [ν(–CO–O–), ϵ = 762 liter/mole-cm for free-radical PMMA] and 1668 cm^{-1} [ν(–CO–C_6H_5), ϵ = 375 liter/mole-cm for anionic PMAP], respectively. The two bands may overlap, and peak separation and peak measurements were carried out graphically and by planimetry.

^{1}H-NMR spectroscopy was run on a Varian HA 100 spectrometer. The spectra obtained in trifluoroacetic acid solution at 30°C at concentration $\simeq$ 10% (w/v), TMS as internal standard, were analyzed by planimetry for PMMA and PMAP contents by using the $-OCH_3$ (singlet at 3.30 ppm) and $-C_6H_5$ (multiplet centered at 7.10 ppm) resonances according to the Eqs. (1) and (2)

$$\text{Molar fraction PMMA} = 10I(-OCH_3)/[(3I(\text{Total H}) + 2I(-OCH_3)] \qquad (1a)$$

or

$$= 5I(-OCH_3)/[5I(-OCH_3) + 2I(-C_6H_5)] \qquad (1b)$$

$$\text{Molar fraction PMAP} = 8I(-C_6H_5)/[5I(\text{total H}) - 2I(-C_6H_5)] \qquad (2a)$$

or

$$= 3I(-C_6H_5)/[5I(-OCH_3) + 3I(C_6H_5)] \qquad (2b)$$

Flash pyrolysis was carried out by Curie point pyrolysis (induction heating of the filament up to its Curie point in 30 msec) on a Fisher apparatus. The pyrolysis of 20 μg of copolymer (deposited upon the filament as a film from 2 μl of a 1% solution in chloroform or acetone) was carried out at 700°C for 3 sec. The separation and analysis of the degradation products was performed by using the same chromatographic technique as for kinetic measurements.

Molecular Weights

Number-average molecular weights were measured by osmometry for $\overline{M}_n \geq 1.5 \times 10^4$ on toluene solutions at 35°C with a Mechrolab 52 high-speed membrane osmometer, Schleicher and Schuell SS08 cellulose acetate membranes, or Ultracella Allerfeinst membranes (Membrane Filter Gesellschaft) or by tonometry for $\overline{M}_n < 1.5 \times 10^4$

on benzene solutions at 35°C with a Hewlett-Packard 302 vapor-pressure osmometer.

RESULTS AND DISCUSSION

In presentation of the results the following abbreviations have been used: MMA = monomer A; MAP = monomer B (M = A + B); I = initiator (AIBN); f_A and f_B = molar fractions of A and B in the monomer feed; F_A and F_B = molar fractions of A and B in the copolymer; x and n = A/B ratios in the monomer feed and in the copolymer, respectively.

The gas chromatographic method applied to solution copolymerization leads to conversion curves defined with good accuracy, and allows measurements of the various rates d[A]/dt, d[B]/dt and d[DA]/dt at any time of the reaction, and thus the determination of the instantaneous copolymer composition [8, 9], especially of the initial copolymer (t → 0).

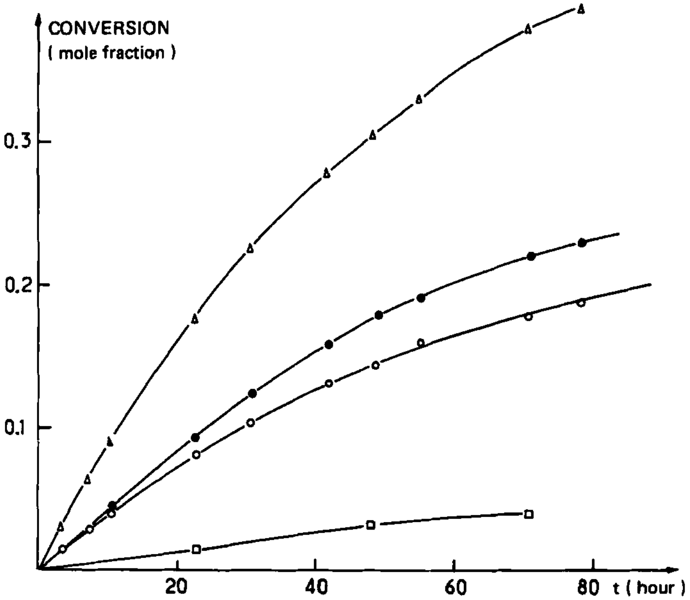


FIG. 1. Conversion curves for solution copolymerization (run 13, Table 2): (△) MMA; (●) total MAP; (○) MAP in copolymer; (□) MAP in DA.

TABLE 1. Analytical Data on Noninitial Copolymers

	Molar fraction of MAP in copolymer F_B				
Run[a]	Elemental analysis	UV	H^1-NMR	IR	Flash pyrolysis
2	0.0708	0.0675			
3	0.0925	0.0843	0.0851		0.095
11	0.223	0.219	0.218		0.211
12	0.285	0.272			
13	0.318	0.302			
14	0.393	0.380	0.378	0.367	0.362
23	0.769	0.755		0.763	

[a] See Tables 2 and 3 for the initial conditions of the copolymerizations.

The recovered low conversion samples (yield ≤ 6%) have been analyzed through independent techniques; some characteristic results are collected in Table 1. The analytical data obtained from elemental analysis, ^{1}H-NMR and UV spectroscopy are in good agreement over the whole range of composition. UV and IR analysis rest on the assumption that the molar absorptivity of the chromophoric units in the copolymer is independent of the monomer unit distribution along the chain and has the same value as in the parent homopolymer taken as reference; this is not always true [10, 11], but for MMA-MAP copolymers this assumption is quite verified. Thus, UV spectrometry has been used for bulk copolymers. On the other hand PMMA, PMAP, and the MMA-MAP copolymers quantitatively depolymerize at 700° C to yield the corresponding monomers. This feature may be considered as a strong argument for a regular head-to-tail placement of monomer units in the anionic PMAP (in good agreement with previous results [6]) and in the radical MMA-MAP copolymers as well.

The experimental results of solution and bulk copolymerizations are collected in Tables 2 and 3, respectively.

Diels-Alder Condensation Product

In Table 4 are collected our experimental results related to thermal condensation of MAP in bulk at 60° C together with literature data [6].

TABLE 2. Solution Copolymerization of MMA and MAP at 60° C

Run	Concentration of reactants, (mole/liter)			f_A	Copolymerization rates (mole/liter-sec × 10^6)[a]		F_A[b]	$\overline{M}_n \times 10^{-3}$
	[A]	[B]	[I]		d[A]/dt	d[B]/dt		
1	5.302	0.282	0.0625	0.949	210.8	6.15	0.972	32.9
2	3.917	0.493	0.0581	0.888	80.5	5.32	0.938	14.8
3	4.846	0.803	0.0552	0.858	67.6	5.84	0.920	17.6
4	6.013	1.001	0.0642	0.857	68.1	5.96	0.919	22.1
5[c]	6.018	1.052	0.0632	0.851	66.5	5.85	0.919	22.0
6[c]	6.013	1.042	0.0635	0.852	67.9	5.80	0.922	22.2
7[d]	3.563	0.883	0.0457	0.801	34.1	4.50	0.883	
11	2.767	1.776	0.0411	0.609	12.2	3.50	0.777	9.05
13[d]	2.339	2.299	0.0507	0.504	6.40	2.72	0.701	5.55
20	0.463	4.164	0.0451	0.100	0.75	1.34	0.360	
21	0.232	4.447	0.0479	0.0495	0.49	1.2	0.294	

[a] Initial rates of copolymerization for t → 0.

[b] Composition of the initial copolymer for t → 0.

[c] Copolymerization in presence of initially added DA: [DA]/[M] = 0.001 and 0.02 for runs 5 and 6.

[d] Solvent, toluene. Solvent in all other cases is ethylbenzene.

TABLE 3. Bulk Copolymerization of MMA and MAP at 60° C

Run	Concentration of reactants (mole/liter) [A]	[B]	[I]	f_A	Polymerization time, (hr)	Yield (%)	F_A	$\overline{M}_n \times 10^{-3}$
8	6.993	1.791	0.090	0.796	0.5	2.6	0.884	
9	6.486	2.170	0.102	0.749	1.3	3.0	0.859	18.8
10	5.451	2.943	0.087	0.649	2	2.4	0.806	
12	4.548	3.618	0.084	0.557	3	1.8	0.728	
14	2.906	4.884	0.142	0.375	66	35.5	0.622	8.20
15	2.690	5.006	0.153	0.349	10	1.0	0.598	
16	2.276	5.315	0.138	0.300	27	5.8	0.550	4.90
17	1.650	5.783	0.151	0.222	8	0.33	0.508	
18	1.110	6.186	0.135	0.152	35.5	2.1	0.439	3.08
19	0.973	6.289	0.151	0.134	65	5.0	0.415	
22	0.720	6.478	0.150	0.10	67	0.9	0.323	
23	0.312	6.782	0.071	0.046	164	4.2	0.245	

TABLE 4. Diels-Alder Condensation of MAP

Temperature (°C)	Time t (hr)	Conversion α^a	$k_c \times 10^6$ (sec^{-1})^b
60^c	120	0.404	1.20
60^c	164	0.516	1.23
60^c	303	0.758	1.30
75^d	144	0.538	1.49
80^d	187	0.734	1.97
85^d	117	0.520	1.74
90^d	304	0.945	2.65

[a] Calculated as $\alpha = ([B]_0 - [B]_t/[B]_0$.

[b] From $k_c = 1/t \times \log[1/1 - \alpha)]$.

[c] Our experimental data.

[d] Data of Mulvaney et al. [6].

Formation of Diels-Alder (DA) condensation product obeys first-order kinetics with respect to MAP:

$$\frac{d[DA]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

$$= \frac{1}{2} k_c[B] \qquad (3)$$

$$\log[1/(1 - \alpha)] = k_c t \qquad (4)$$

where $k_c = 1.25 \times 10^{-6}$ sec^{-1} at 60° C.

In a first approximation, k_c values at higher temperatures may be calculated from the literature data [6] (no kinetic studies but single point experiments); all the k_c values thus obtained correlate poorly on an Arrhenius plot, leading to a rough estimate of an activation energy $E \simeq 4.9 \pm 0.9$ kcal/°C-mole.

In the copolymerization experiments, Diels-Alder condensation and copolymerization are simultaneous and competitive processes; their relative rates depend on monomer and initiator concentrations. For solution reaction, DA condensation is much slower than expected from a kinetic equation of the form $d[DA]/dt = 0.625 \times 10^{-6}\ [M]\ f_B$; for an equimolar feed of MMA and MAP (run 13 in Table 2 and Fig. 1), the initial rate of MAP consumption to yield DA is about 0.12 of the total rate of MAP consumption. For constant [A], [B], and [I], we have checked the possible influence of DA onto the MMA-MAP copolymerization by introducing 0.001 and 0.02 mole fraction of DA with respect to total monomers in the initial solution (runs 5 and 6 of Table 2). Neither the kinetics nor the number-average molecular weight of the copolymer ($\overline{M}_n = 2.2 \times 10^4$ for 0.25 conversion after 8 hr) are affected by the presence of DA in the monomer solution. DA is not an inhibitor, a retarder, or a transfer agent and it may be considered as an inert diluent in copolymerization. The Diels-Alder condensation, which is a one-step multicenter cycloaddition [12], does not interfere directly with the free-radical copolymerization process, but it is effective as a simultaneous reaction competing with copolymerization for MAP consumption.

Copolymerization Rate R_p and Number-Average Degree of Polymerization $\overline{DP}_n$

The influence of the molar fraction of MAP in the monomer feed on the copolymerization rate R_p and on the number-average degree of polymerization $\overline{DP}_n$ may be studied with the following assumptions.

For a fixed monomer ratio, R_p and $\overline{DP}_n$ depend on monomer and initiator concentration according to Eqs. (5) and (6) [13]:

$$R_p = K[M][I]^{0.5} \qquad (5)$$

$$\overline{DP}_n = K'[M]/[I]^{0.5} \qquad (6)$$

$\overline{DP}_n$ values are deduced from the corresponding values of $\overline{M}_n$ taking into account the copolymer composition:

$$\overline{M}_n = \overline{DP}_n m \tag{7}$$

where

$$m = m_A F_A + m_B F_B \tag{8}$$

where m_A and m_B are the molecular weights of the monomeric units A and B respectively.

The R_p and $\overline{DP}_n$ values for MMA homopolymerization at 60° C were calculated from literature data [14] according to:

$$R_p \text{ (mole/liter-sec)} = 3.39 \times 10^{-4} \; [A] \; [I]^{0.5}$$

$$1/\overline{DP}_n = 2.66 \times 10^{-2} \; [I]^{0.5} / [A] + 0.7 \times 10^{-5} + c_S [S]/[A]$$

For solution copolymerization, the variations of R_p versus f_B, normalized to [I] = 0.0543 mole/liter and [M] = 5.43 mole/liter are plotted in Fig. 2. R_p is a drastically decreasing function of f_B, chiefly for low f_B values; R_p is reduced by a factor greater than 2 when f_B increases from 0 to 0.05.

The variations of $\overline{DP}_n$ versus f_B, normalized to [I] = 0.083 mole/liter and [M] = 6.40 mole/liter are plotted in Fig. 3. All the experimental points may reasonably fit a single curve, but the $\overline{DP}_n$ values seem systematically higher for bulk than for solution copolymerization, in spite of the normalization procedure. This slight discrepancy may reflect the fact that the solvent ethylbenzene is actually a transfer agent towards growing chains terminated by MMA (transfer constant $C_T = 7.66 \times 10^{-5}$ at 60° C [15]) or possibly MAP radicals. The average degree of polymerization decreases markedly when the molar fraction of MAP in the monomer feed increases, especially for low MAP contents; $\overline{DP}_n$ is divided by a factor of 4 when f_B increases from 0 to 0.10.

The parallel decrease of R_p and $\overline{DP}_n$ when f_B increases is probably characteristic of the low propagation constant and of the high termination constants of MAP-terminated growing chains.

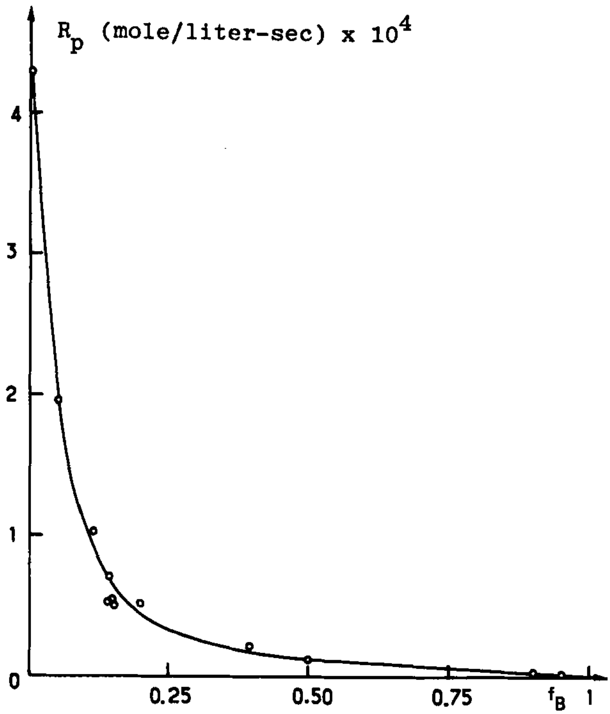


FIG. 2. Variation of the copolymerization rate R_p vs. f_B for solution copolymerizations normalized to [I] = 0.0543 mole/liter and [M] = 5.43 mole/liter.

Determination of the Reactivity Ratios

Whenever necessary, the instantaneous composition of the monomer feed in equilibrium with the copolymer has been corrected for the MAP consumed in the DA condensation.

As pointed out by Guyot et al. [9], r_A and r_B may be deduced from the analysis of a single copolymerization experiment at various degrees of conversion. The Fineman- Ross linearization method [16] (Appendix I, Fig. 4) applied to our experiment 13 in Table 2 ($f_A \simeq f_B \simeq 0.5$; Fig. 1) leads to $r_A = 1.675 \pm 0.002$, $r_B = 0.160 \pm 0.001$.

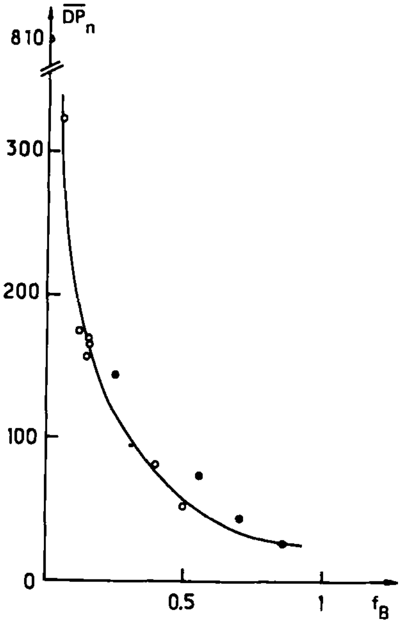


FIG. 3. Variation of the number-average degree of polymerization DP_n vs. f_B for (●) bulk and (○) solution copolymerizations normalized to [I] = 0.083 mole/liter and [M] = 6.40 mole/liter.

These values can be considered only a rough estimate because of the low range of compositions covered in a single experiment (x decreases only from 1.017 to 0.759).

We have determined the reactivity ratios from the analytical data for the initial copolymers obtained in solution and for the low conversion (≤6%) bulk copolymers by using both the Fineman-Ross and the Yezrielev-Brokhina-Roskin [17] (YBR) methods; this last procedure linearizes the experimental data through symmetrical equations (Appendix II) and gives more accurate and more reliable results [18]. The different values of the reactivity ratios are collected in Table 5. The Fineman-Ross and YBR methods lead to slightly different but compatible reactivity ratios, the YBR values generally being higher than the Fineman- Ross values; the YBR determination must be preferred [18].

It is not necessary to take into account separately solution and bulk copolymerizations. There is no discontinuity when going from

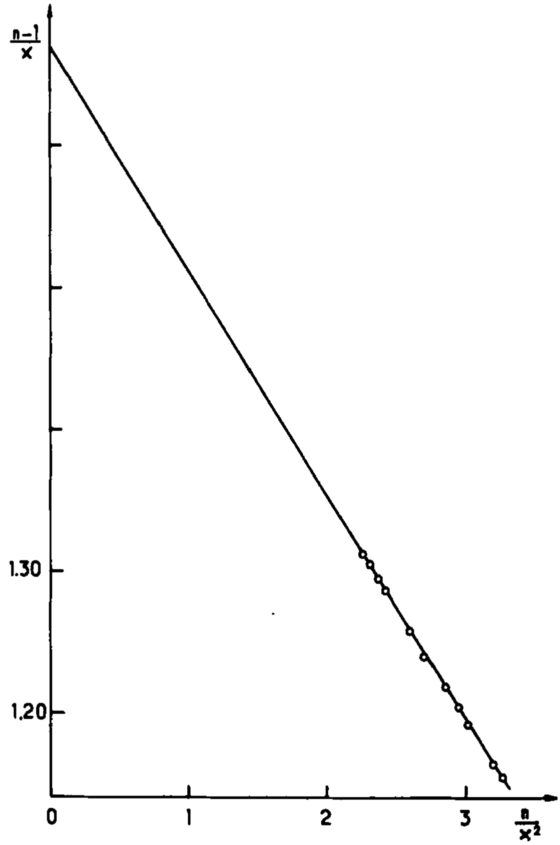


FIG. 4. Fineman-Ross plot for solution copolymerization (run 13, Table 2) analyzed at different degrees of conversion.

ethylbenzene solution to pure monomers, the growing chains remaining soluble throughout the copolymerization in the reaction medium in both cases. There is apparently no significant effect of monomer concentration between 4.41 and 8.79 mole/liter.

In the whole range of monomer feed composition ($0.05 \leq f_A \leq 0.95$) all the experimental results may reasonably be taken into account with a single pair of reactivity ratios $r_A = 1.77 \pm 0.02$, $r_B = 0.11 \pm 0.006$ in spite of a less satisfying agreement between analytical data and calculated curve for $0.25 \leq f_A \leq 0.50$ (Fig. 5).

TABLE 5. MMA (r_A) and MAP (r_B) Reactivity Ratios at 60° C

	FR method		YBR method	
Monomer feed range	r_A	r_B	r_A	r_B
Solution copolymerization				
$0.05 \leq f_A \leq 0.95$	1.62 ± 0.19	0.086 ± 0.004	1.78 ± 0.03	0.095 ± 0.010
$0.20 \leq f_A \leq 0.95$	1.83 ± 0.03	0.208 ± 0.036	1.81 ± 0.03	0.184 ± 0.064
Bulk copolymerization				
$0.04 \leq f_A \leq 0.80$	1.57 ± 0.07	0.113 ± 0.002	1.73 ± 0.04	0.120 ± 0.006
$0.20 \leq f_A \leq 0.80$	1.77 ± 0.06	0.165 ± 0.011	1.80 ± 0.04	0.172 ± 0.017
Solution and bulk copolymerization				
$0.04 \leq f_A \leq 0.95$	1.52 ± 0.18	0.098 ± 0.004	1.77 ± 0.02	0.110 ± 0.006
$0.20 \leq f_A \leq 0.95$	1.79 ± 0.03	0.168 ± 0.007	1.81 ± 0.02	0.174 ± 0.015
$0.20 \leq f_A \leq 0.80$	1.77 ± 0.05	0.165 ± 0.009	1.79 ± 0.03	0.170 ± 0.015

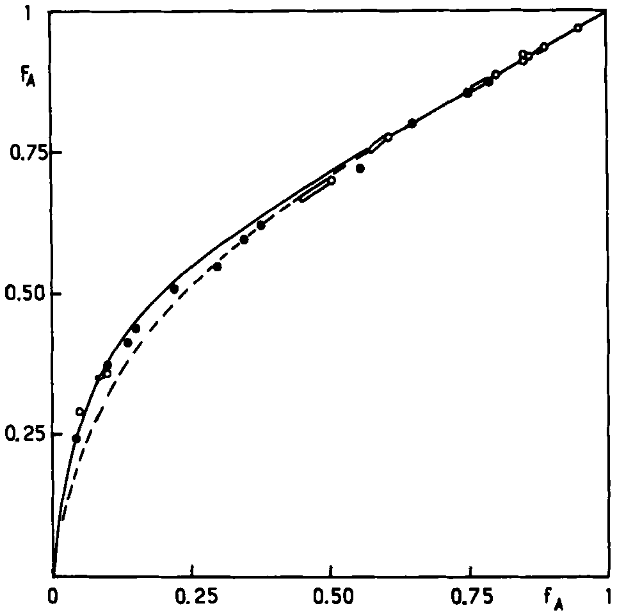


FIG. 5. Composition diagram for terminal unit model: (●) bulk copolymers at low conversion; (○) initial (t → 0) copolymers; (▭) copolymers obtained at various degrees of conversion from the same monomer feed solution; (——) calculated curve for $r_A = 1.775$, $r_B = 0.110$ ($0.05 \leq f_A \leq 0.95$); (---) calculated curve for $r_A = 1.810$, $r_B = 0.174$ ($0.20 \leq f_A$).

On the other hand, the characteristic inability of MAP to undergo homopolymerization suggests that the copolymerization can be perturbed by propagation-depropagation equilibrium or by penultimate effects, as it is often the case with α,α'-disubstituted ethylenes of high steric hindrance. These deviations from the terminal unit model are expected to occur for MAP-rich monomer feeds, such as $f_A < 0.2$, for instance. The reactivity ratio r_A is practically independent of the range of monomer feed composition selected for its determination, $r_A \simeq 1.80$; the corresponding r_B value significantly increases from 0.110 to 0.174 when the domain of MAP-rich monomer feed ($f_A \leq 0.2$)

is excluded from the calculation. The two composition curves derived from the two pairs of reactivity ratios corresponding to $f_A \geq 0.2$ and $f_A \geq 0.05$ are clearly distinct for $f_A \leq 0.3$ and they allow a better fit of the experimental data in their own range of monomer feed composition (Fig. 5). Because of this slight ambiguity we have tried to check if it is not possible to choose another copolymerization scheme, in order to get an optimized agreement between the experimental data and the calculated composition curve over the whole range of monomer feed composition.

Copolymerization with Depropagation

The effect of a propagation-depropagation equilibrium on copolymer composition has received much attention [19], and Lowry's theory [20] (Appendix III) has been successfully applied to a number of systems, α-methylstyrene–styrene or α-methylstyrene–acrylonitrile, for instance [21]. We have tried to test it according to the following assumptions.

The constant K of the MAP propagation-depropagation equilibrium at 60° C may be calculated from the limiting copolymer composition F_B when $f_A \to 0$:

Lowry's Case I:

$$K = \frac{2F_B - 1}{F_B} \; \frac{1}{[B]}$$

deduced directly from Lowry's equations [20];

Lowry's Case II:

$$K = \frac{3F_B - 2}{2F_B - 1} \; \frac{1}{[B]}$$

according to O'Driscoll et al. [21].

By extrapolation of the experimental data, the limiting F_B value when $f_A \to 0$ may be estimated around 0.85. The calculated K values are respectively 0.12 and 0.18 for bulk ([B] = 7.016 mole/liter) and solution ($[B]_{max}$ = 4.44 mole/liter) copolymerizations in both cases I and II. These values are obviously very rough but useful approximations, since the composition equations are only slightly sensitive to appreciable variations of K.

Lowry's case I

MAP has an appreciable tendency to depolymerize whenever it is attached to another MAP unit

$$\sim\sim ABB\cdot \rightleftharpoons \sim\sim AB\cdot + B$$

For bulk copolymerization, the composition curve calculated by using Lowry's equations and the set of values $r_A = 1.81$, $r_B = 0.174$ ($f_B \leq 0.8$), K = 0.12 does not agree well with the experimental results (Fig. 6).

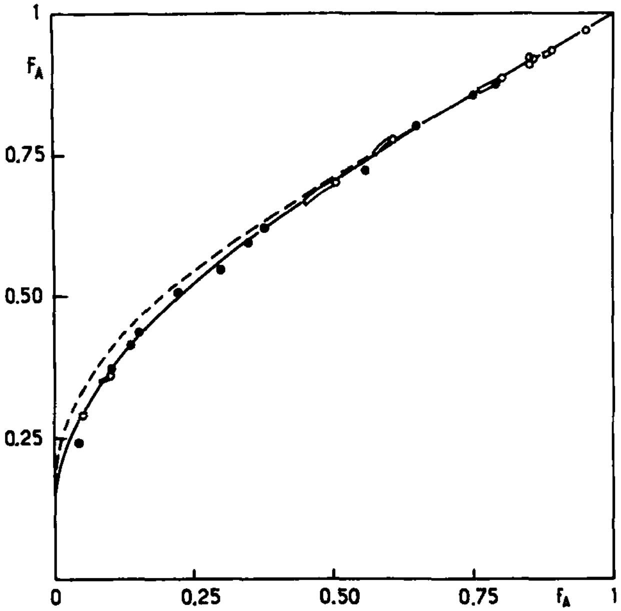


FIG. 6. Composition diagram for copolymerization with depropagation ($r_A = 1.81$, $r_B = 0.174$, K = 0.12–0.18): experimental points as in Fig. 5; (--) calculated curve according to Lowry's first case; (——) calculated curve according to Lowry's second case.

Lowry's Case II

MAP has an appreciable tendency to depolymerize whenever it is attached to a sequence of two or more MAP units:

$$\sim\sim\sim ABBB\cdot \rightleftharpoons ABB\cdot + B$$

The composition curves for bulk (K = 0.12) and solution (K = 0.18) copolymerizations are identical and allow a good fit of the experimental results over the whole range of monomer feed composition (Fig. 6).

Nevertheless this improved agreement between experimental results and theoretical curve was not taken as a strong argument in favor of this model, because of the previous assumptions. A study of a "possible" MAP homopolymerization (ceiling temperature, propagation-depropagation equilibrium constant) and of the influence of temperature and concentration on copolymerization would be necessary to ascertain the process of copolymerization with depropagation. Moreover it has been recently shown that even for monomer pairs such as styrene–α–methylstyrene at 60° C, where depropagation of α-methylstyrene is not doubtful (ceiling temperature = 61° C, K = 0.110 for pure α-methylstyrene at 60° C [22]) the classical terminal unit model may quite conveniently take into account all the copolymerization data [23].

Copolymerization with Penultimate Effects

Penultimate effects [24-26] have often been proposed to explain some deviations from the simple terminal unit model occurring in the extreme ranges of monomer feed composition, especially with monomers unable to undergo homopolymerization [27]. Starting with $r_A = 1.79$, $r_B = 0.170$, values related to the medium composition range $0.2 \leq f_A \leq 0.8$, and applying the classical iteration method [28] (Appendix IV), first for MAP ($f_B \geq 0.65$) and then for MMA ($f_A \geq 0.85$), we have determined the following values of the four reactivity ratios:

$r_{AA} = 1.77 \pm 0.02$

$r_{BA} = 2.30 \pm 0.10$

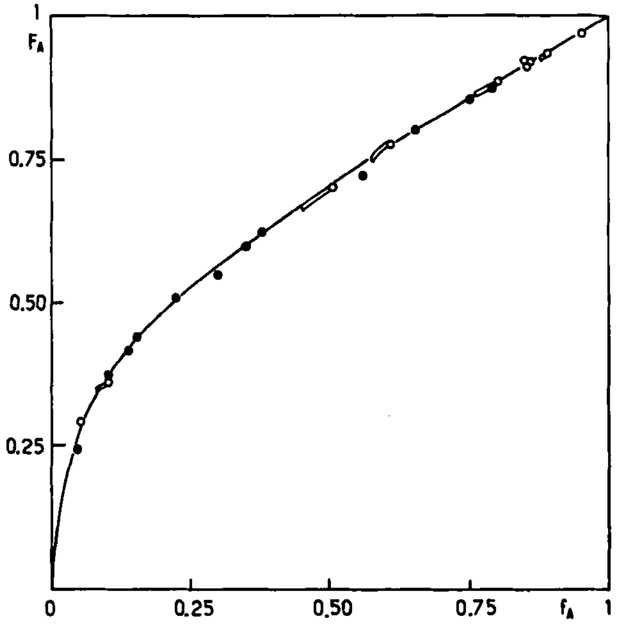


FIG. 7. Composition diagram for copolymerization with penultimate effects: experimental points as in Fig. 5; (——) calculated curve for $r_{AA} = 1.77$, $r_{BA} = 2.30$, $r_{BB} = 0.058$, $r_{AB} = 0.325$.

$$r_{AB} = 0.325 \pm 0.03$$

$$r_{BB} = 0.058 \pm 0.01$$

There is excellent agreement between the experimental data and the composition curve calculated from these ratios over the whole range of monomer feed composition ($0.05 \leq f_A \leq 0.95$) (Fig. 7).

As pointed out recently by Guyot [29], the penultimate effects may represent "only an increase of the number of mathematical parameters of the copolymerization equations which allow a better fit of the experimental data." In our case, strong interactions between monomers MMA and MAP, both having strongly electron-deficient double bonds are probably excluded; no solvent effect is apparent, but preferential or selective solvation of the growing macroradicals by a given monomer still remains possible. This point would require further work, but this is beyond the scope of the present study.

Structure–Reactivity Relationship for MAP through the Q-e Scheme

In Table 6 we give different values of the Q and e parameters [30, 31] for MAP estimated by three different methods: from styrene-MAP reactivity ratios recalculated from literature data [6] according to the YBR method [17] : $r_S = 0.23$, $r_B = 0.27$; from our own values of the MMA-MAP reactivity ratios: $r_A = 1.77$, $r_B = 0.11$ ($0.05 \leq f_A \leq 0.95$); from the Q and e values of acrylophenone (AP) [32], which has the structure $CH_2{=}CH{-}CO{-}C_6H_5$ (AP) : Q = 1.40 and e = 0.74. The introduction of an α-methyl group on the double bond of AP may be expected to lead respectively to an increase of Q and a decrease of e values, measured by $\Delta \log Q \simeq 0.26$ and $\Delta e \simeq -0.25$ [33-35]. These assumptions, chiefly that reflecting the influence of substitution on e values, are obviously very rough but useful approximations to correlate structure and monomer reactivity.

The Q and e values of MAP calculated from styrene-MAP copolymerization do not show the expected variations with respect to the corresponding values of acrylophenone; nevertheless, they may appear still plausible, taking into account the very low accuracy of

TABLE 6. Q and e Parameters of MAP

		MAP			
	AP[a]	From Q and e values of AP	From sty–MAP copolymerization[b]	From MMA-MAP copolymerization[c]	
Q	1.40	2.55	1.14	0.70	0.25
e	0.74	0.49	0.87	1.68	-0.88

[a] Data of Otsu and Tanaka [32].
[b] Styrene: Q = 1.0, e = -0.8.
[c] MMA: Q = 0.74, e = 0.40 [33].

the reactivity ratios ($0.18 \leq r_S \leq 0.50$, $0.12 \leq r_B \leq 0.35$) [6] and the semiquantitative character of the previous assumptions. On the other hand, MMA-MAP copolymerization data lead to two pairs of Q and e values which may be considered very improbable. It is well known that the Q-e scheme may not be valid in the case of sterically hindered 1,1-disubstituted ethylenes [30, 31, 33-35], and MAP reactivity is probably more dependent on steric hindrance, which is not taken into account in the Q-e scheme, than on resonance (Q) and polarity (e) factors. In the case of MMA-MAP copolymerization, steric factors are obviously of greater influence than in the styrene-MAP copolymerization; the Q and e values deduced from MMA-MAP reactivity ratios probably have no real physical meaning. Finally, the polymerizability of MAP by anionic initiation [6] and its inability to undergo free-radical homopolymerization are consistent with the assumption that the monomer reactivity depends more on steric than on electronic factors [34].

CONCLUSION

In spite of the simultaneous and competitive Diels-Alder condensation of MAP, MMA and MAP may be readily copolymerized either in bulk or in solution, by free-radical initiation. At 60° C, over the whole range of monomer feed investigated ($0.05 \leq f_A \leq 0.95$), the copolymerization process may be reasonably taken into account by using the classical terminal unit model. Because of the inability of MAP to undergo homopolymerization under the same experimental conditions, we have tentatively tested two more sophisticated models, copolymerization with depropagation (affecting MAP macroradicals) and copolymerization with penultimate effects. Both models lead to a slightly better agreement between experimental data and calculated composition curves. Nevertheless, the composition data alone do not allow us to select a physical basis for these assumptions. The unit distribution in the chain, which has been shown to be sensitive to depropagation [36] and penultimate effects [37] will be studied in a forthcoming communication [38].

The free-radical copolymerization does not allow a good control of important parameters such as molecular weight or molecular weight distribution and stereoregularity. Nevertheless it is the easiest method of synthesis of MMA-MAP copolymers in a large range of composition, since the reaction of phenyllithium on well defined PMMA fails to introduce selectively MAP units in the PMMA backbone [39]. The free-radical copolymers may be considered useful models for photodegradation studies. Preliminary work on our samples has been achieved by Professor Guillet and his co-workers [40].

APPENDIX I

Linearization Method of Fineman and Ross [16] for Calculating Reactivity Ratios

$$(n - 1)/x = r_A - (n/x^2)r_B$$

where

$$x = f_A/f_B$$

$$n = F_A/F_B$$

APPENDIX II

Analytical Method for Calculating Reactivity Ratios According to Yezrielev, Brokhina, and Roskin [17]

$$r_A = \frac{\lambda_B \mu_A + N \mu_B}{\lambda_A \lambda_B - N^2} \pm \sqrt{\frac{\Delta^2 \lambda_B}{\lambda_A \lambda_B - N^2}}$$

$$r_B + \frac{\lambda_A \mu_B + N \mu_A}{\lambda_A \lambda_B - N^2} \pm \sqrt{\frac{\Delta^2 \lambda_A}{\lambda_A \lambda_B - N^2}}$$

where N is the number of copolymerization experiments and

$$\lambda_A = \sum_{i=1}^{N} (x_i^2/n_i)$$

$$\lambda_B = \sum_{i=1}^{N} (n_i/x_i^2)$$

$$\mu_A = \sum_{i=1}^{N} [x_i(n_i - 1)/n_i]$$

$$\mu_B = \sum_{i=1}^{N} [(1 - n_i)/x_i]$$

$$\Delta^2 = \sum_{i=1}^{N} \Delta_i^{\,2}/(N - 2)$$

with

$$\Delta_i^{\,2} = \left(r_A \sqrt{\frac{x_i^{\,2}}{n_i}} - r_B \sqrt{\frac{n_i}{x_i^{\,2}}} - \sqrt{n_i} + \frac{1}{\sqrt{n_i}} \right)^2$$

APPENDIX III

Effect of Depropagation on Copolymer Composition According to Lowry [20]

A has a negligible tendency to depolymerize and K is the ratio of the propagation and depropagation rates for macroradicals B:

$$\alpha = \frac{\left[1 + K[B] + (K/r_B)[A]\right] - \left\{ \left[1 + K[B] + (K/r_B)[A]\right]^2 - 4K[B] \right\}^{1/}}{2}$$

$$\gamma = \frac{\{ K[B] + (K/r_B)[A] - \alpha \}}{K[B]}$$

Case 1: B has an appreciable tendency to depolymerize whenever it is attached to another B unit:

$$\sim\sim\sim ABB^{\bullet} \rightleftharpoons \sim\sim\sim AB^{\bullet} + B$$

$$F_B = \frac{[B]}{r_A[A]\,(1 - \alpha) + [B]\,(2 - \alpha)}$$

Case 2: B has an appreciable tendency to depolymerize whenever it is attached to a sequence of two or more B units

$$\sim\!\sim\!\sim\!\sim ABBB\cdot \rightleftharpoons \sim\!\sim\!\sim\!\sim ABB\cdot + B$$

$$F_B = \frac{\beta\gamma - 1\,[1/(1-\beta)^2]}{\{(r_A[A]/[B]) + 1\}\{\beta\gamma + [\beta/(1-\beta)]\} + \beta\gamma - 1 + [1/(1-\beta)^2]}$$

APPENDIX IV

Influence of Penultimate Effects on Copolymer Composition and Estimation of Reactivity Ratios

$$n = \frac{d[A]}{d[B]}$$

$$= \frac{1 + r_{BA}\,x(r_{AA}\,x + 1)/(r_{BA}\,x + 1)}{1 + (r_{AB}/x)(r_{BB} + x)/(r_{AB} + x)}$$

where

$$r_{AA} = k_{AAA}/k_{AAB}$$

$$r_{BA} = k_{BAA}/k_{BAB}$$

$$r_{BB} = k_{BBB}/k_{BBA}$$

$$r_{AB} = k_{ABB}/k_{ABA}$$

According to Barb [27] and assuming that the reactivity of B radicals is null or for monomer feeds such as $x = [A]/[B] \rightarrow \infty$, the composition equation is reduced to the linear form:

$$r_{AA} = [(n - 2)/x] + (1/r_{BA})[(n - 1)/x^2]$$

which allows determination of the reactivity ratios r_{AA} and r_{BA} by using a Fineman-Ross plot. When r_{BB} and $r_{AB} \neq 0$ and x has a finite value, the general composition equation may be used if we take for the first step of calculation $r_{BB} = r_{AB} = r_B$, where r_B is the reactivity ratio determined in the case of a terminal unit model. Rough values of r_{AA} and r_{BA} are first determined for monomer feed very rich in monomer A. Then the same calculations related to r_{BB} and r_{AB} are performed for monomer feeds very rich in B, using the previously found values of r_{AA} and r_{BA}. After one or two iterations, the method leads to the four reactivity ratios with a reasonable accuracy [28].

ACKNOWLEDGMENTS

The authors are indebted to Dr. P. Rempp for his continuous interest for this work and for his critical discussion of the manuscript.

REFERENCES

[1] Y. Amerik and J. E. Guillet, Macromolecules, 4, 375 (1971).
[2] E. Dàn and J. E. Guillet, Macromolecules, 6, 230 (1973).
[3] M. Kato and Y. Yoneshige, Makromol. Chem., 164, 159 (1973).
[4] F. J. Golemba and J. E. Guillet, Macromolecules, 5, 212 (1972).
[5] A. R. Lyons, J. Polym. Sci., Macromol. Rev. Ed., 6, 251 (1972).
[6] J. E. Mulvaney, J. G. Dillon, and J. L. Laverty, J. Polym. Sci. A-1, 6, 1841 (1968).
[7] J. H. Burckhalter and R. C. Fuson, J. Amer. Chem. Soc., 70, 4184 (1948).
[8] H. J. Harwood, H. Baikowitz, and H. F. Trommer, paper presented at American Chemical Society Meeting, 1963; Polym. Preprints, 4 (1), 133 (1963).
[9] A. Gyot and J. Guillot, J. Chim. Phys., 1964, 1434.
[10] H. J. Harwood, Angew. Chem. Int. Ed., 4, 1051 (1965).

[11] B. M. Gallo and S. Russo, J. Macromol. Sci. Chem., A8, 521 (1974).

[12] J. B. Sauer, Angew. Chem. Int. Ed., 6, 16 (1967).

[13] T. Alfrey Jr., J. J. Bohrer, and H. Mark, Copolymerization, Interscience, New York, 1952, p. 197.

[14] J. L. O'Brien and F. Gornick, J. Amer. Chem. Soc., 77, 4757 (1955).

[15] R. N. Chadha, J. S. Shulka and G. S. Misra, Trans. Faraday Soc., 53, 240 (1957).

[16] M. Fineman and S. D. Ross, J. Polym. Sci., 5, 269 (1950).

[17] A. I. Yezrielev, E. L. Brokhina and Ye. S. Roskin, Polym. Sci. USSR, 11, 1894 (1969).

[18] R. M. Joshi, J. Macromol. Sci.–Chem., A7, 1231 (1973).

[19] H. Sawada, J. Macromol. Sci.–Revs. C 10, 293 (1974).

[20] G. G. Lowry, J. Polym. Sci., 42, 463 (1960).

[21] K. F. O'Driscoll and F. P. Gasparro, J. Macromol. Sci.–Chem., A1, 643 (1967).

[22] D. J. Worsfold and S. Bywater, J. Polym. Sci., 26, 299 (1957).

[23] A. Rudin and S. S. M. Chiang, J. Polym. Sci. Polym. Chem. Ed., 12, 2235 (1974).

[24] E. Merz, T. Alfrey, and G. Goldfinger, J. Polym. Sci., 1, 75 (1946).

[25] F. P. Price, J. Chem. Phys., 36, 209 (1962).

[26] G. E. Ham, in Copolymerization, G. E. Ham, Ed., Interscience-Wiley, New York, 1964, p. 1.

[27] W. G. Barb, J. Polym. Sci., 11, 117 (1953).

[28] J. Guillot, Quad. Ric. Sci., 84, 189 (1973).

[29] A. Guyot, paper presented at 23rd International Symposium on Macromolecules, IUPAC, Madrid, Sept. 15-20, 1974.

[30] T. Alfrey Jr., J. J. Bohrer, and H. Mark, Copolymerization, Interscience, New York, 1952, pp. 45 and 79.

[31] T. Alfrey Jr. and L. J. Young, in Copolymerization, G. E. Ham, Ed., Interscience-Wiley, New York, 1964, p. 67.

[32] T. Otsu and H. Tanaka, Polymer, 16, 468 (1975).

[33] G. E. Ham, in Encyclopedia of Polymer Science and Technology, Wiley-Interscience, New York, 1966, Vol. 4, p. 165.

[34] M. Imoto and T. Tsuruta, in Structure and Mechanism of Vinyl Polymerization, T. Tsuruta and K. F. O'Driscoll Eds., Dekker, New York, 1969, pp. 1, 27.

[35] T. Otsu, in Progress in Polymer Science Japan, Wiley (Halsted Press), New York, 1971, Vol. 1, p. 1.

[36] J. A. Howell, M. Izu, and K. F. O'Driscoll, J. Polym. Sci. A-1, 8, 699 (1970).

[37] M. Berger and I. Kuntz, J. Polym. Sci. A, 2, 1687 (1964).

[38] R. Roussel and J. C. Galin, J. Macromol. Sci.–Chem., in press.
[39] R. Roussel and J. C. Galin, to be published.
[40] J. E. Guillet, personal communication.

Accepted by editor December 15, 1975
Received for publication December 23, 1975