



STUDY OF RADICAL METHYL METHACRYLATE–METHACRYLIC ACID COPOLYMERIZATION IN ISOPROPYL ALCOHOL BY DYNAMIC LASER SCATTERING AND ^{13}C -NMR SPECTROSCOPY

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(Received 1 July 1993; accepted in final form 10 January 1994)

Abstract—The copolymerization of methyl methacrylate and methacrylic acid in isopropyl alcohol is studied by kinetic, dynamic laser scattering and ^{13}C -NMR methods. Correlations are established between the dependence of the copolymerization rate, the apparent average molecular weight, the diffusion coefficients and the configurational triad composition on the monomer feed. These correlations and the fact that both copolymerization constants are smaller than unity ($r_{\text{MMA}} = 0.63 \pm 0.03$; $r_{\text{MA}} = 0.25 \pm 0.05$) are in good agreement with the assumption that a comonomer complex takes part in the propagation reaction. A new Markov chain method for the estimation of the configurational triad mole fraction which accounts for the complex participation in a macromolecule formation is developed. Qualitative criteria for evidence the participation of the comonomer complex in copolymerization are proposed using experimental and terminal model calculated mole fractions of the compositional triads and diads.

INTRODUCTION

Methyl methacrylate (MMA) and methacrylic acid (MA) copolymers are widely used filmforming materials, bindings in the production of paints and varnishes [1]. There are particularly strict requirements for the compositions, molecular weight and molecular weight and compositional distributions of the MMA–MA copolymers when they are used in the pharmaceutical industry [2]. For this reason the regulation of the process of MA copolymerization with the view to obtaining copolymers with controlled values of the above characteristics is a question of present interest. It has been established that the nature of the solvent [3–5], the monomer concentrations [6], and the presence of metal ions and basic additives [7, 8] in the copolymerization medium influence considerably the copolymerization rate and the elementary rate constants. Though π -electron systems of both comonomers are identical, it is possible to achieve a considerable deviation from the expected ideal copolymerization ($r_{\text{MMA}} = r_{\text{MA}} = 1$) by changing the factors mentioned above. A probable reason for this effect is the formation of H-bonds (H-complexes) between the molecules of one of the comonomers and the molecules of the other comonomer, the solvents and special additives. For example, the values of two copolymerization constants are considerably lower than unity ($r_{\text{MA}} = 0.50 \pm 0.03$; $r_{\text{MMA}} = 0.43 \pm 0.02$) as a result of the H-complex formation between MA and nitrogen bases added to the copolymerization medium [8]. This effect is explained by an increase in

the MA electron donor properties which results in the formation of the MMA–MA donor–acceptor complex. The assumption is that the participation of this complex in the chain propagation is responsible for the increase in the alternating tendency and, hence, for the decrease in the copolymerization constant values. This tendency and the decrease in the copolymerization reactivity ratios can be explained by the essential increase in the cross-propagation rate constants ($k_{\text{MA,MMA}}$; $k_{\text{MMA,MA}}$). The third possible explanation for the described results is a combination of the two mechanisms mentioned above. Thus a part of the copolymer macromolecule is formed by the complex addition to the propagating end and the other part by the addition of free monomers. A knowledge of this chain propagation mechanism is a necessary condition for the effective regulation of copolymerization.

Considerable deviation from ideal behavior for MMA–MA copolymerization in isopropyl alcohol (IPA) is established in this work. The extremal character of the dependence of the copolymerization rate and the apparent molecular weight of the resultant copolymers on the monomer feed is in accordance with the assumption that donor–acceptor complexes (DAC) between the two comonomers participate in the chain propagation. The initial suggestion is that both comonomers form H-complexes with the solvents. These assumptions are confirmed by the results from the analysis of the configurational and compositional microstructures of the product copolymers, determined by ^{13}C -NMR spectroscopy.

EXPERIMENTAL PROCEDURES

Materials

MMA (Fluka), MA (Janssen) and AIBN (Merck) were used in this study, IPA and methyl alcohol were used after being distilled.

Radical MMA-MA copolymerization

MMA-MA copolymers were prepared by radical copolymerization in IPA (monomer concentration 25% w/w) at 70° and AIBN (1% w/w based on total comonomers) as an initiator. The conversion is <10 wt%, based on total comonomers. The synthesized copolymers were isolated by a precipitation in diethyl ether and purified by double dissolution and precipitation IPA and diethyl ether, respectively. The mole fraction of MA in the product copolymers was determined by titration of the 1% (w/w) copolymer solution in acetone with a 0.1% (w/w) solution of sodium hydroxide and phenolphthalein as an indicator. The copolymerization constant values were calculated by the Kelen-Tudos [9] and Yesrielev-Brokhina-Roskin [10] methods. The copolymerization rate was determined gravimetrically.

Dynamic laser scattering measurements

Static and dynamic characteristics of the product copolymers were determined by the Malvern system 4700 C equipment for laser scattering measurements ensured with an argon laser ($\lambda = 488$ nm) and a 64 canal autocorrelator. The apparent average molecular weight ($M_{w,app}$) of the product copolymers was determined by classical Zimm plot extrapolations [11] using the static regime of the system. Copolymer solutions in methyl alcohol were used in these measurements. The determined specific refractive index increments of these copolymer solutions are presented in Table 1. The z-average diffusion coefficients (\bar{D}_z) and the hydrodynamic radius (\bar{R}_{zh}) of the copolymer macromolecules were calculated following the autocorrelation functions obtained when the system was used in the dynamic regime [12].

 ^{13}C -NMR spectra measurements

The natural abundance ^{13}C -NMR spectra of copolymer solutions (10–15% w/w) in d_6 -dimethylsulphoxide were registered with 10 mm probe on a BRUCKER WP 80 spectrometer operating at 20 MHz in the pulsed FT-mode with a wide band modulated proton decoupling. TMS was employed as an internal standard. The probe temperature under the experimental conditions was 25°C. Spectrometer parameters for the determination of the spectra were: 4 kHz spectral width, 1 sec data acquisition time, 3 sec delay between the repetitive pulses. Typically 14,000–16,000 free induction decays were accumulated for each quantitative determination. Spectra were obtained under a fully proton-decoupled scheme in which the proton decoupler was off during 3.0 sec delay time and gated on at the start of the 1.0 sec acquisition period. In this way, problems associated with the differential nuclear Overhauser enhancement for different carbonyl carbons were avoided [13]. Peak separation was carried out graphically and peak area measurements by planimeter.

Table 1. Specific refractive index increments of the MMA-MA copolymer solutions in methyl alcohol with different mole fractions of MA at 25°C

No.	M_{MA}	m_{MA}	$\frac{dn}{dc} \left(\frac{\text{cm}^3}{\text{g}} \right)$
1	0.30	0.40	$0.22857 \pm 8 \cdot 10^{-5}$
2	0.40	0.52	$0.20317 \pm 6 \cdot 10^{-5}$
3	0.50	0.55	$0.18214 \pm 9 \cdot 10^{-5}$
4	0.60	0.64	$0.17971 \pm 9 \cdot 10^{-5}$
5	0.70	0.72	$0.16315 \pm 7 \cdot 10^{-5}$
6	0.80	0.76	$0.16057 \pm 5 \cdot 10^{-5}$
7	0.90	0.82	$0.15761 \pm 6 \cdot 10^{-5}$

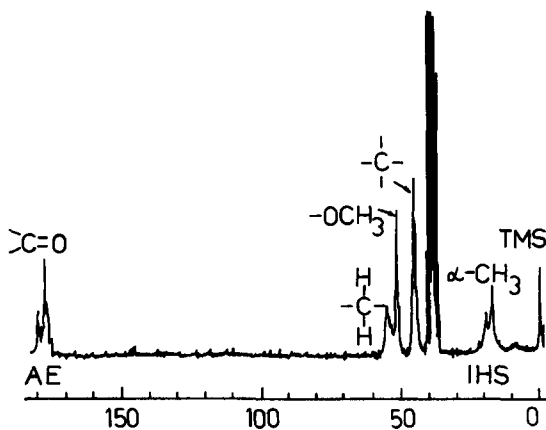


Fig. 1. ^{13}C -NMR spectrum of MMA-MA copolymer, obtained in IPA. The mole fraction of MA in the copolymer is 0.32. Temperature: 25°C. Solvent $-d_6$ -DMSO. Copolymer concentration: 15% (w/v).

One of the ^{13}C -NMR spectra of the MMA-MA copolymers (mole fraction of MA in the copolymer is 0.32) is presented in Fig. 1. The general peak groups of all the spectra similar to the presented one were assigned to the carbon atoms in the two types of monomer units in the copolymers [14]. d_6 -DMSO carbon resonance peaks are situated in the area around 40 ppm. Three peaks of the α -CH₃ resonance region (16–22 ppm) were assigned to the three types of configurational triads in the copolymers. Each of them is denoted by I, S or H in Fig. 1. The areas of these peaks were used in the determination of the mole fraction of iso-, syndio- and heterotriads in copolymers [P(i), P(s), P(h)]. The probability for a mesoaddition of the comonomers to the propagating ends P_m was calculated from the P(i), P(s) and P(h) values:

$$P_m = \sqrt{P(i)} = 1 - \sqrt{P(s)} = \frac{1 - \sqrt{2P(h)}}{2}$$

P_m was used in the calculation of the configuration pentad mole fractions F_{mmmm} , F_{mmmr} , F_{rrmm} , F_{rrmr} , F_{rrmm} , F_{rrrm} , F_{mrrr} , F_{rrrr} , F_{mrrr} , F_{mrrm} etc. (m = mesoaddition and r = racemic addition): $F_{mmmm} = P_m^4$; $F_{mmmr} = P_m^3(1 - P_m)$; $F_{mrrm} = P_m^2(1 - P_m)^2$ etc.

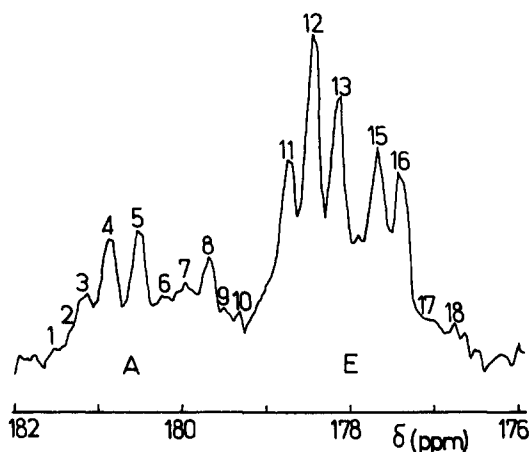


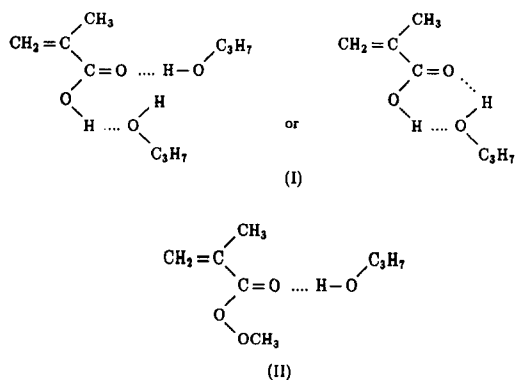
Fig. 2. ^{13}C -NMR spectrum of the carbonyl region atom of MMA-MA copolymer, obtained in IPA. The mole fraction of MA in the copolymer is 0.32. Temperature: 25°C. Solvent $-d_6$ -DMSO. Copolymer concentration: 15% (w/v).

A higher resolution ^{13}C -NMR spectrum of the carbonyl region from 175 to 182 ppm is shown in Fig. 2. It supplies most of the information necessary for the determination of the compositional triads in the copolymer macromolecules. The peaks in the range from 179.5 to 182 ppm are assigned to the MA carbonyl resonances and the peaks from 175 to 179 ppm to the MMA carbonyl resonances [15]. The peaks of this 18-band spectrum are assigned to different 128 pentad-configurational-triadcompositional combinations of sequences in the copolymer macromolecules [16–19]. The intensity of these peaks (I_k ; $k = 1, \dots, 18$) can be presented as a sum of the corresponding configurational-compositional sequences $I_k = \sum_i \sum_r P(y_1 X_1 y_2 X_2 y_3 X_3 y_4)$ ($k = 1, \dots, 18$; $X_1, X_2, X_3 = \text{MA, MMA}$, and $y_1, y_2, y_3, y_4 = m, r$) [20]. Since these mole fractions can be presented as products of the probabilities for the realization of the corresponding configurational and compositional sequences $P(y_1 X_1 y_2 X_2 y_3 X_3 y_4) = P(X_1 X_2 X_3) P(y_1 y_2 y_3 y_4)$ [18, 21], the mole fractions of the compositional triads [$P(X_1 X_2 X_3)$] are calculated from the system of the algebraic equations $P_k = \sum_i \sum_r P(X_1, X_2, X_3) P(y_1 y_2 y_3 y_4)$; $k = 1, \dots, 18$ [14–19].

RESULTS AND DISCUSSION

Copolymerization reactivity ratios

Dependence of the MMA-MA copolymer composition on the comonomer feed is shown in Fig. 3. The copolymerization reactivity ratios calculated in terms of these data by the Kelen-Tüdös method [9] are $r_{\text{MMA}} = 0.63 \pm 0.03$ and $r_{\text{MA}} = 0.25 \pm 0.05$, and by the Yesrielev-Brokhina-Roskin method— $r_{\text{MMA}} = 0.58 \pm 0.09$ and $r_{\text{MA}} = 0.29 \pm 0.08$. Due to the identical π -electron systems of the two comonomers the copolymerization reactivity ratios must be equal to unity in the framework of the ideal reactivity theory of radical polymerization [22]. The fact that both experimental values of the copolymerization constants are considerably lower than unity indicates an alternation tendency in the copolymerization in IPA.



This tendency can be explained by the inequality of the π -electron densities of the two comonomers caused by the different types of H-complexes (I and II) formed between the comonomers and IPA. The formation of the second H-bond between the MA carboxyl group and IPA (in addition to the bond in the MMA-IPA H-complex) results in a small ionization of this group and a relative increase in the MA-double bond electron density. It is important that this change of the electron density is in the opposite direction to that caused by the H-bond

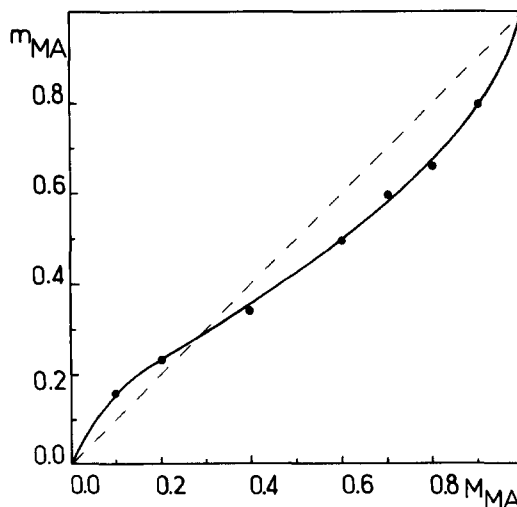


Fig. 3. Dependence of MA mole fraction in MMA-MA copolymers on MA mole fraction in monomer feed. Solvent: IPA. Temperature: 70°C. $C_{\text{AIBN}} = 1\%$.

formed between the carbonyl oxygen atom and IPA. This difference in the π -electron density of the two comonomer molecules is just the necessary condition for a donor-acceptor interaction between comonomer molecules. But the formation of the DAC was not proved by U.V.-, I.R.- and ^1H -NMR spectroscopy. Though the DAC registration is difficult probably due to the small value of the equilibrium constant of complex formation the DAC participation in the copolymer chain propagation cannot be excluded [23]. A possible test which could prove such a participation is the study of the changes in the copolymerization rate caused by variations in the monomer feed.

Dependence of the initial copolymerization rate on the monomer feed

The variation of the initial copolymerization rate as a function of the comonomer feed and of the total monomer concentration is shown in Fig. 4. There

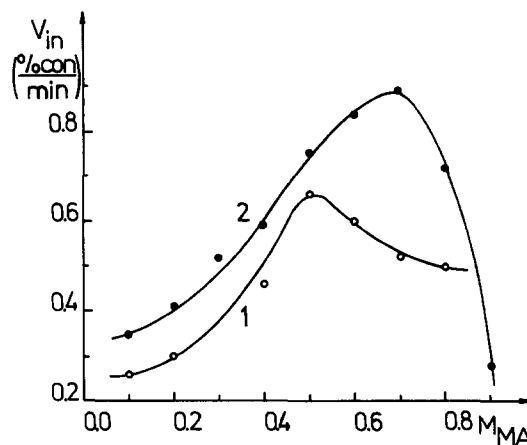


Fig. 4. Dependence of the initial copolymerization rate on the monomer feed at total comonomer concentration 17.5% (w/v) (1) and 25.0% (w/v) (2). Temperature: 70°C. $C_{\text{AIBN}} = 1\%$.

are three features of this dependence which confirm indirectly the DAC participation in the formation of the copolymer chain: the extremal character of the resultant curves [24], the appearance of the curve maximum near the equimolar comonomer composition [24, 25] and the shift of the maximum disposition when the total monomer concentration is changed [26]. These features as well as the established inequalities $r_{MA} < 1$ and $r_{MMA} < 1$ are the most commonly used criteria for DAC participation in the copolymer macromolecular formation [27]. Hence, it is interesting to study the influence of the monomer feed on the molecular characteristics of the product copolymers.

Molecular characteristics of the synthesized copolymers

The dependence of the apparent average weight molecular weight ($\bar{M}_{w,ap}$), z-average values of the diffusion coefficients (\bar{D}_z) and the hydrodynamic radius ($\bar{R}_{z,h}$) of the copolymer macromolecules on the monomer feed are shown in Fig. 5. The \bar{M}_w values are called "apparent" because they can be determined by the Zimm method [11]. Since the conversion is small enough the copolymer composition inhomogeneity is small too and the resultant average molecular weights are fairly close to the real ones [28].

As it has been mentioned above, one of the important peculiarities of the above dependence is its extremal character. It is essential to notice that the extrema of this dependence coincide with those of the dependence of the copolymerization rate on the monomer feed (curve 2, Fig. 4). This coincidence is not an accidental one and can be explained by the generalized statistical analysis of the molecular weight distribution [29]. In accordance with this approach the number molecular weight distribution

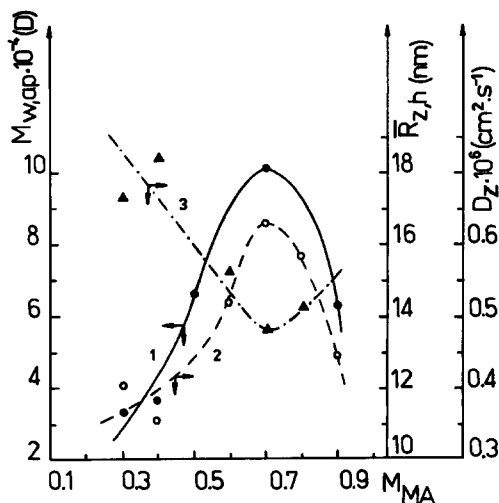


Fig. 5. Dependence of the apparent average weight molecular weight ($\bar{M}_{w,ap}$, curve 1), z-average hydrodynamic radius ($\bar{R}_{z,h}$, curve 2) of the macromolecules and z-average diffusion coefficients (\bar{D}_z , curve 3) of the MMA-MA copolymers, obtained in IPA, on the monomer feed. Total monomer concentration: 25% (w/v).

Table 2. Dependence of the mole fractions of the configurational triads P(i), P(s), P(h), the constant $\rho = 2[m]/[r]/[mr]$, Bernoulian criterion ($Be = 4[mm]/[rr]/[mr]^2$) and the coisotacticity probability P_m of the MMA-MA copolymers, obtained in IPA, on the mole part of MA in monomer feed (M_{MA}). Temperature: 70°C. Comonomer concentration: 25%, (w/v)

No.	M_{MA}	m_{MA}	P(i)	P(h)	P(s)	P_m	Be	ρ
1	0.10	0.17	0.03 ₅	0.35 ₂	0.61 ₃	0.20 ₃	0.70	0.92
2	0.30	0.32	0.03 ₈	0.32 ₂	0.64 ₀	0.20 ₃	0.92	0.99
3	0.70	0.57	0.04 ₃	0.30 ₆	0.64 ₈	0.20 ₁	1.17	1.04
4	0.80	0.66	0.04 ₀	0.32 ₁	0.63 ₉	0.20 ₁	0.99	1.00

function is $q_n(M) = \alpha \exp(-\alpha M)$, where α is the ratio of the termination rate (V_t) to the propagation rate (V_p) of copolymerization ($\alpha = V_t/V_p$). Using this function it is easy to show that $\bar{M}_w = 2/\alpha$ since

$$\bar{M}_w = \frac{\int_0^\infty M^2 \alpha \exp(-\alpha M) dM}{\int_0^\infty M \alpha \exp(-\alpha M) dM} = \frac{1}{\alpha} \frac{\Gamma(3)}{\Gamma(2)} = \frac{2}{\alpha} \quad (1)$$

where $\Gamma(x)$ is a Gamma function. As the total copolymerization rate $V_t \sim 1/\alpha$, it is clear why the curve $\bar{M}_{w,ap}$ vs M_{MA} (curve 1, Fig. 5) follows curve 2 in Fig. 4. The \bar{D}_z values correlate with those of $\bar{M}_{w,ap}$ while \bar{D}_z is inversely proportional to $\bar{R}_{z,h}$ in accordance with the Stox law [12]. It is clear from this analysis that the dependence presented in Fig. 3 is not a fundamentally new proof of the DAC participation in the chain propagation. This dependence is a direct consequence of curve 2 in Fig. 4. This result necessitates a study of the dependence of the configurational and compositional macromolecule triads on the monomer feed.

Configurational triad composition of the obtained copolymers

The mole fractions of the iso-[P(i)], syndio-[P(s)] and hetero-[P(h)] configurational triads of the product copolymer macromolecules, calculated from the α -CH₃ resonance peak areas at 16.30, 18.45 and 20.80 ppm [13, 19], are presented in Table 2. It is clear that the P(i), P(s) and P(h) values vary little with the mole fraction of MA in the monomer feed (M_{MA}). The established relationships are extremal in this case too. This non-linear dependence shows that the configurational sequence formation cannot be described by the classical Bernoulian scheme. The considerable deviations of the ρ and Be values from unity confirm this assumption. Therefore it is interesting to discuss the possible reasons for the established non-linearity. One of them is the difference between the mesoaddition probabilities of the comonomers to the propagating chains ($P_{m,MA} \neq P_{m,MMA}$). It is possible to show that with this provision the P(i), P(s) and P(h) dependence on the mole fraction of one of the comonomers (m_{MMA} in this case) is quadratic.

$$P(i) = [P_{m,MA} + m_{MMA}(P_{m,MMA} - P_{m,MA})]^2 \quad (2)$$

$$P(s) = [1 - P_{m,MA} + m_{MMA}(P_{m,MA} - P_{m,MMA})]^2 \quad (3)$$

$$P(h) = 2[1 - P_{m,MA} + m_{MMA}(P_{m,MA} - P_{m,MMA})].$$

$$\times [P_{m,MA} + m_{MMA}(P_{m,MMA} - P_{m,MA})]. \quad (4)$$

According to equation (3) if $P_{m,MA} > P_{m,MMA}$ then $P(s)$ should increase with the increasing of m_{MMA} . Conversely when $P_{m,MA} < P_{m,MMA}$, $P(i)$ should increase with the increasing of m_{MMA} . However, the experimental dependence (Table 2) is not in an agreement with these consequences thus invalidating the above reason as a basis for the established non-linearity. The same conclusion follows from the equivalence of the two comonomer π -electron systems [18].

Another reason for the established deviation from the Bernoulian scheme is the addition of the comonomer complex to the propagating copolymer

The probability of the second step is assumed to be unity. This separation generalizes the two fields of the random events of the configurational triad formation either by a comonomer complex or single comonomer molecule addition to the propagating chain. This generalization allows the configurational triad formation with the comonomer complex participation to be described by a second order regular Markov chain with four additional states mm_1 , mr_1 , rm_1 , rr_1 . Each of these corresponds to a state of the propagating chain obtained after the addition of the first complex component to the active ends. Moreover, this separation allows the mesoaddition probabilities to the propagating chains to be distinguished for both comonomer molecules ($P_{m,r}$) and for the first or the second complex components ($P_{m,c1}$ and $P_{m,c2}$). If the values of all these probabilities are different the transition matrix P (5) of the Markov chain discussed above is formed.

$$P = \begin{matrix} & \begin{matrix} mm & mm_1 & mr & mr_1 & rm & rm_1 & rr & rr_1 \end{matrix} \\ \begin{matrix} mm \\ mm_1 \\ mr \\ mr_1 \\ rm \\ rm_1 \\ rr \\ rr_1 \end{matrix} & \begin{bmatrix} (1-P_c)P_{m,f} P_c P_{m,c1} (1-P_c)(1-P_{m,f}) P_c(1-P_{m,c1}) & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ P_{m,c2} & 0 & 1-P_{m,c2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & (1-P_c)P_{m,f} P_c P_{m,c1} (1-P_c)(1-P_{m,f}) P_c(1-P_{m,c1}) & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & P_{m,c2} & 0 & 1-P_{m,c2} & 0 \\ (1-P_c)P_{m,f} P_c P_{m,c1} (1-P_c)(1-P_{m,f}) P_c(1-P_{m,c1}) & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ P_{m,c2} & 0 & 1-P_{m,c2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & (1-P_c)P_{m,f} P_c P_{m,c1} (1-P_c)(1-P_{m,f}) P_c(1-P_{m,c1}) & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & P_{m,c2} & 0 & 1-P_{m,c2} & 0 \end{bmatrix} \end{matrix} \quad (5)$$

macromolecules with a probability P_c . Such an addition changes considerably the mechanism of the configurational triad formation. These changes cannot be expressed by the Bernoulian scheme. In fact configurational diads from the penultimate and last monomer units of the propagating chain are formed when single comonomer molecule add to the active ends, while configurational triads are formed from the above units and the first complex component when the comonomer complex takes part in the propagation reaction. This difference requires the application of another model, different from the Bernoulian scheme, for an estimation of the mole fractions of the configurational triads. The application of the second order regular Markov chain with states corresponding to different configurational triads (mm , mr , rm and rr) holds out such a possibility [30]. The advantages of this approach is that it permits expression of the triad formation in terms of the two mechanisms mentined above. For that purpose the addition of the comonomer complex to the active ends is separated into two consecutive steps.

The average life times of the Markov chain in different states (F_{mm} , F_{mm1} , F_{mr} , F_{mr1} , F_{rr} , F_{rr1} , F_{rm} , F_{rm1}) form a vector \mathbf{F} . Their values can be determined by the equations $\mathbf{F}P = \mathbf{F}$ and $\sum_i F_i = 1$ [31]. The mole fractions of the configurational triads

$$P(i) = F_{mm} + F_{mm1} \quad (6)$$

$$P(s) = F_{rr} + F_{rr1} \quad (7)$$

$$P(h) = F_{mr} + F_{rm} + F_{mr1} + F_{rm1} \quad (8)$$

and the contribution of the comonomer complex in the copolymer macromolecule formation $[P(c)]$

$$P(c) = 2(F_{mm1} + F_{mr1} + F_{rr1} + F_{rm1}) = \frac{2P_c}{1 + P_c} \quad (9)$$

can be determined very easily in this way.

If $0 < P_c < 1$ and $P_{m,f} \neq P_{m,c1} \neq P_{m,c2}$ then

$$P(i) = \frac{[(1 - P_c)P_{m,f} + P_c P_{m,c1}][(1 - P_c)P_{m,f} + P_c P_{m,c2}] + P_c P_{m,c1} P_{m,c2}}{1 + P_c} \quad (10)$$

$$P(s) = \frac{[(1 - P_c)(1 - P_{m,f}) + P_c(1 - P_{m,c1})][(1 - P_c)(1 - P_{m,f}) + P_c(1 - P_{m,c2})]}{1 + P_c} + \frac{P_c(1 - P_{m,c1})(1 - P_{m,c2})}{1 + P_c} \quad (11)$$

$$P(h) = 2 \frac{[(1 - P_c)(1 - P_{m,f}) + P_c(1 - P_{m,c1})][(1 - P_c)P_{m,f} + P_c P_{m,c2}]}{1 + P_c} + \frac{P_c P_{m,c1}(1 - P_{m,c2})}{1 + P_c} \quad (12)$$

Considering the dependence of P_c on the monomer feed

$$P_c = \frac{(k_{A,CA} + k_{A,CB})[C]}{(k_{A,CA} + k_{A,CB})[C] + k_{A,A}[A] + k_{A,B}[B]} + \frac{(k_{B,CA} + k_{B,CB})[C]}{(k_{B,CA} + k_{B,CB})[C] + k_{B,A}[A] + k_{B,B}[B]} \quad (13)$$

the equations (10)–(12) show the complex non-linear variation of $P(i)$, $P(s)$ and $P(h)$ as a function of the monomer feed. With $k_{A,A}$, $k_{A,B}$, $k_{B,A}$, $k_{B,B}$, $k_{A,CA}$, $k_{A,CB}$, $k_{B,CA}$ and $k_{B,CB}$ in the last equation (13) the rate constants of the comonomer (A and B) and their complex (C) additions to both propagating radicals ($\sim \dot{A}$ and $\sim \dot{B}$) are denoted. It is important to note that C can add to these radicals from both faces.

It is easy to show by the suggested method that non-linear dependence between P_c and the mole fractions of the configurational triads (monomer feed respectively) are valid in the cases when $P_{m,c1} = P_{m,c2} \neq P_{m,f}$ or $P_{m,f} = P_{m,c1} \neq P_{m,c2}$. The linear dependence between $P(i)$, $P(s)$, $P(h)$ and $P(c)$ can be obtained only if all of the mesoaddition probabilities are uniform ($P_{m,c1} = P_{m,c2} = P_{m,f}$). The configurational triad formation in this case follows the Bernoulian scheme. Hence if $P_c \neq 0$ the deviation from the Bernoulian scheme should decrease with decreasing differences between $P_{m,c1}$, $P_{m,c2}$ and $P_{m,f}$. The consequences of this conclusion for the MMA–MA copolymerization discussed above are that $P_c \neq 0$ and there exist slight differences between $P_{m,c1}$, $P_{m,c2}$ and $P_{m,f}$. It is in agreement with the assumption made in the earlier sections for DAC

participation in the copolymer macromolecular formation. Thus it is necessary to check the validity of this assumption by analysis of the copolymer compositional triad composition.

Copolymer compositional triad composition

The experimental mole fractions of all possible compositional triads in three of the analyzed copolymers are presented in Table 3. Because of the small percentage of MA (B) in the first copolymer in Table 2 and poor peak resolution in the resonance region for the B-centered triads, the compositional triad composition of this copolymer was not determined. In Table 4 the experimental values of the compositional triads are compared with values calculated by the terminal model (using Bovey statistics [32]), accounting only for the participation of single comonomer molecules in the propagation reaction. According to this model which does not consider the comonomer complex participation in the propagation reaction $m_{AAA} = m_A P_{AA}^2$; $m_{AAB} = 2m_A P_{AA} P_{AB}$; $m_{BAB} = m_B P_{BA} P_{AB}$; $m_{BBB} = m_B P_{BB}^2$; $m_{BBA} = 2m_B P_{BB} P_{BA}$ and $m_{ABA} = m_A P_{AB} P_{BA}$ where the conventional probabilities P_{AA} , P_{AB} , P_{BB} and P_{BA} can be calculated from the copolymerization constants and comonomer concentrations in the monomer feed:

$$P_{AA} = \frac{r_A[A]}{r_A[A] + [B]}; \quad P_{AB} = 1 - P_{AA};$$

$$P_{BB} = \frac{r_B[B]}{r_B[B] + [A]}; \quad P_{BA} = 1 - P_{BB}.$$

Table 3. Variation of the experimental mole fractions of the compositional triads of the MMA(A)–MA(B) copolymers, obtained in IPA, at 70 °C

No.	M _B	m _B	m _{BBB}	m _{BBA}	m _{ABA}	m _{AAA}	m _{AAB}	m _{BAB}
1	0.30	0.32	0.01	0.16	0.15	0.14	0.45	0.09
2	0.70	0.57	0.10	0.36	0.11	0.02	0.23	0.18
3	0.80	0.66	0.19	0.39	0.08	0.01	0.16	0.18

Table 4. Terminal model calculated mole fractions of the MMA(A)–MA(B) copolymer compositional triads and the conventional probability (P_{AA} and P_{BB}) values

No.	M _B	m _B	m _{BBB}	m _{BBA}	m _{ABA}	m _{AAA}	m _{AAB}	m _{BAB}	P _{AA}	P _{BB}
1	0.30	0.32	0.00	0.06	0.26	0.23	0.33	0.12	0.57 <sub2< sub=""></sub2<>	0.11 <sub0< sub=""></sub0<>
2	0.70	0.57	0.09	0.28	0.22	0.01	0.11	0.29	0.15 <sub6< sub=""></sub6<>	0.40 <sub3< sub=""></sub3<>
3	0.80	0.66	0.19	0.33	0.14	0.00	0.07	0.27	0.12 <sub7< sub=""></sub7<>	0.53 <sub7< sub=""></sub7<>

The relative percentage differences between the calculated $[(m_{ijk})_{calc}]$ and experimental $[(m_{ijk})_{exp}]$ values of the compositional triads:

$$\Delta\% = \frac{(m_{ijk})_{calc} - (m_{ijk})_{exp}}{(m_{ijk})_{exp}} 10^2$$

are presented in Table 5. It is clear that there are considerable differences between the experimental and the calculated, by the terminal model, values of the compositional triads. It is important that the calculated mole fractions values of the heterotriads (m_{BBA} and m_{AAB}) are smaller than the experimental ones while the experimental mole fraction values for the alternating triads are smaller than the calculated ones. This inversion is an additional proof of the comonomer complex participation in the copolymer macromolecule formation. In fact, as a result of the participation of such complexes in the propagation reaction the alternating tendency of the monomer units in the resultant copolymer macromolecule should increase. As a consequence the copolymerization constants values, calculated by the Mayo-Lewis equation, should be smaller than the true ones. According to the definition equations for the conventional probabilities a decrease of these values leads to a decrease of P_{AA} and P_{BB} and an increase of P_{AB} and P_{BA} . The final effect is the apparent increase of the alternating triad mole fractions: $m_{ABA} = m_A P_{AB} P_{BA}$ and $m_{BAB} = m_B P_{BA} P_{AB}$. Since this increase is at the expense of the mole fraction values of the other non-alternating compositional triads, the calculated values of the latter are smaller than the experimental ones. It seems probable that this inversion is a common feature of copolymerizations involving comonomer complex participation in the propagation reaction and should be considered as a specific criterion for such participation.

It is interesting to note that the above criterion can also be formulated at a diad level: the heterodiad (AB) mole fraction values, calculated by the terminal model, in copolymer macromolecules formed by comonomer complex participation in the propagation reaction are larger than experimental ones. Using the data in Tables 3 and 4 it is easy to check this form of the above criterion for copolymerization as $m_{AB} = m_{ABA} + m_{BAB} + 0.5(m_{AAB} + m_{BBA})$. From the comparison of these values (Table 6) it is clear that the new form of the criterion is satisfied for the three copolymers analyzed. This is further evidence of comonomer complex participation in the

Table 6. Experimental and terminal model calculated heterodiad mole fractions (m_{AB}) for three, copolymers of MMA (A) and MA (B) obtained in IPA at 70°C

No.	M_B	m_B	$(m_{AB})_{exp}$	$(m_{AB})_{calc}$
1	0.30	0.32	0.54 _s	0.57 _s
2	0.70	0.57	0.58 _s	0.70 _s
3	0.80	0.66	0.52 _s	0.61 ₀

propagation reaction of MMA-MA copolymerization in IPA.

CONCLUSIONS

The most striking feature of the above results is the correlation between the initial copolymerization rate (Fig. 4), the molecular characteristics of the product copolymers (Fig. 5) and the configurational triad composition of the copolymer macromolecules (Table 1) and the monomer feed of the MMA-MA copolymerization in IPA. The analysis of these results shows that this feature as well as the copolymerization constant values can be reasonably explained by the assumption that comonomer complex takes part in the propagation reaction. The formation of this complex is probably a result of the different influence of the H-complexes between the comonomers (MA and MMA) and the solvent (IPA) on the comonomer π -electron densities. This assumption is strongly supported by the results of the analysis of the triad and diad compositions of the product copolymers. The positive differences between the terminal model calculated and the experimental mole fractions of the alternating triads and heterodiad are established and form the basis of the evidence in favour of the above assumption.

In addition the above correlation shows that comonomer complex participation in the propagation reaction influence both the copolymerization characteristics and the copolymer molecular properties and microstructure. Therefore this participation should be considered in order to achieve an effective copolymerization regulation with a view to synthesizing MMA-MA copolymers with desired properties.

It is important also to note that a new quantitative method for estimation of the configurational triad composition dependence on the monomer feed is developed during the analysis of the comonomer complex participation in the propagation reaction. A new inversion rule for the qualitative proof of the complex participation in the copolymerization is suggested. At the triad level this rule says that the terminal model calculated values of the alternating compositional triads should be greater than the experimental ones while the effect for the heterotriads should be the opposite. According to this rule, at the diad level, the terminal model calculated heterodiad mole fractions should be greater than the experimental ones.

Acknowledgements—The authors wish to thank the Bulgarian National Scientific Foundation for its support of this work as well as Professor J. D. Connolly from the University of Glasgow for the NMR spectra measurements and very useful discussions.

Table 5. The relative percentage differences between the terminal model calculated $[(m_{ijk})_{calc}]$ and experimental $[(m_{ijk})_{exp}]$ values of the compositional triads in three MMA(A)-MA(B) copolymers, obtained in IPA at 70°C

	$\Delta(\%) = \frac{(m_{ijk})_{calc} - (m_{ijk})_{exp}}{(m_{ijk})_{exp}} 10^2$		
Triad	Copolymer 1 $m_B = 0.32$	Copolymer 2 $m_B = 0.57$	Copolymer 3 $m_B = 0.66$
m_{BBB}	-100.0	-10.0	0.0
m_{BBA}	-62.5	-22.0	-15.3
m_{ABA}	60.0	100.0	75.0
m_{AAA}	64.3	-50.0	-100.0
m_{AAB}	-26.7	-52.2	-56.2
m_{BAB}	33.3	61.1	58.8

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