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Cross-linking photocopolymerization of dodecyl methacrylate with oxyethylene glycol dimethacrylates: Kinetics and reactivity ratios

Ewa Andrzejewska*, Elzbieta Socha, Maciej Andrzejewski

Institute of Chemical Technology and Engineering, Poznan University of Technology, Pl. M. Sklodowskiej-Curie 2, 60-965 Poznan, Poland

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Abstract

The photo-induced copolymerization of dodecyl methacrylate (DDM) with five oxyethylene glycol dimethacrylates (OEGDM) was investigated. Effects of the monomer ratio and of the length of dimethacrylate spacer group on the polymerization kinetics, the extent of the after-effect and pendant double bond content in the polymerization product were studied and the reactivity ratios estimated. For systems containing OEGDM with short spacers between the methacrylate groups, R_p^{max} reached the highest value at certain monovinyl/divinyl monomer ratio. This phenomenon was discussed in terms of the behavior of the reaction diffusion parameter (as a function of monomer ratio and conversion). Determination of the reactivity ratios by five calculation methods showed that r_1 (DDM) values were lower than 1 and the r_2 (OEGDM) values were higher than 1 indicating that the polymer formed at the beginning of the reaction is more densely cross-linked than that formed in the final reaction stages.

Keywords: Cross-linking photocopolymerization; Kinetics; Reactivity ratios

1. Introduction

The photopolymerization of multifunctional (meth)acrylate monomers and oligomers is a versatile and an efficient technology, which has found a large number of commercial applications. The polymerization of multifunctional monomers leads to the formation of highly cross-linked insoluble products. The density of the network can be regulated by an addition of a monovinyl monomer. Decreasing the cross-link density allows to reach higher conversion of double bonds and reduce polymerization shrinkage. However, reduction of cross-link density by copolymerization with a monovinyl monomer can lead to an increase in heterogeneity due to a compositional drift associated with different reactivities of the comonomers. The more heterogeneous is a material, the more likely it will have a significantly weaker structure in some regions, potentially causing premature failure [1]. The copolymer composition and its distribution are dependent on the reactivity ratios. Thus, the knowledge of the reactivity ratios for monovinyl/divinyl systems is very important to predict the final properties of the product.

The kinetics of the polymerization of a monovinyl/divinyl monomer system depends to a high degree on the monomer ratio. The main factors controlling such systems are the network density of the polymer being formed and the initial viscosity of the system (when the viscosities of the monomers differ substantially). These factors control the diffusion of the reacting species influencing the termination step from the beginning of the polymerization and determine when the propagation becomes diffusion controlled.

The analysis of the polymerization kinetics of monovinyl/divinyl comonomer systems showed that in some cases the maximum polymerization rate R_p^{max} reaches the highest value at certain monovinyl/divinyl monomer ratio [1–8]. For methacrylate/dimethacrylate systems it was suggested that the increase in R_p^{max} with the increase in the dimethacrylate content (up to reaching the highest R_p^{max} value) is due to enhanced Trommsdorff effect which results from the reduction of the

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* Corresponding author. Tel. +48 61 665 3637; fax: +48 61 665 3649.
E-mail address: ewa.andrzejewska@put.poznan.pl (E. Andrzejewska).

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kinetic-controlled reaction region [2] whereas the subsequent drop of R_p^{max} with further increase of the dimethacrylate content is probably due to propagation becoming diffusion limited at lower conversions [1]. It was also proposed that an increase in cross-link density causes a more abrupt reduction in the termination rate increasing R_p^{max}. However, it should also reduce the initiation efficiency and overall propagation rate coefficient k_p (due to increased fraction of pendant double bonds) reducing the magnitude of R_p^{max} [3]. According to Ref. [4] the main factors to obtain optimum reactivity are the initial resin viscosity and, within a given range of viscosities, structural effects allowing for molecular mobility.

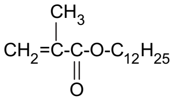
An additional effect on the polymerization kinetics may arise from different reactivities of the monomers used, which are characterized by their reactivity ratios. Even in systems containing only monomers having the same type of functionality, the reactivity ratios can differ from 1 as was found for some methacrylate/methacrylate systems [9–13].

There are many methods of estimation of reactivity ratios, all based on the Mayo–Lewis equation and classified as differential or integral ones [14]. The corresponding equations and solution methods are linear or non-linear. Currently, non-linear methods are recommended [15]. Although a great number of works were devoted to the determination of reactivity ratios in various systems, rather a limited number of them considered monovinyl/divinyl systems [16–25] including methacrylate/dimethacrylate systems [16,18,23–25].

There are two main types of kinetic models for copolymerization of monovinyl with divinyl monomers [23]. In the first case, the normal terminal model is adopted and within this model there are two conventions regarding the calculation of the concentration of divinyl monomer. In the first (1) convention the divinyl monomer is treated completely the same as normal one–double-bond monomers. This approach is the most popular. In the second (2) convention it is assumed that the reactivity of the two double bonds in the divinyl monomer does not change during the reaction and in the classical copolymerization equation the concentration of the divinyl monomer is doubled (but when the copolymer composition is considered, the concentration of the monomer unit of the divinyl monomer remains the same). This means that $r_1(1)=0.5r_1(2)$ and $r_2(1)=2r_2(2)$, where r_1 and r_2 are the reactivity ratios of the monovinyl and divinyl monomers, respectively. Thus, both the conventions are equivalent, when used to describe copolymerization behavior [23]. The second type of kinetic models is more complex and takes the possible difference in the reactivity of monomer and pendant vinyl group along with occurrence of cyclization into consideration. It was indicated, however, that the copolymerization parameters need not be too much distorted when determined from the classical copolymerization equation, despite of deviations of cross-linking copolymerization from linear copolymerization [21,23,26].

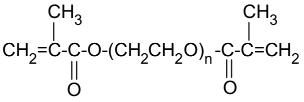
Although the polymerization kinetics of monovinyl/divinyl monomer systems was the subject of many works, a systematic analysis regarding the influence of the concentration and the length of the divinyl monomer along with determination of the reactivity ratios was not made. In this study the photo-induced copolymerization of dodecyl methacrylate (DDM) with a series of oxyethylene glycol dimethacrylates (OEGDM) was investigated (according to Flory's definition, these monomer are bi- and tetrafunctional, respectively [17]). DDM has been chosen as a non-volatile difunctional model monomer. The effects of the monomer ratio and the dimethacrylate spacer group on the polymerization kinetics, the extent of the after-effect and pendant double bond content in the polymerization product were studied and the reactivity ratios were estimated for four DDM/OEGDM systems.

The investigated OEGDM were ethylene glycol dimethacrylate (EGDM, $n=1$), di(ethylene glycol) dimethacrylate (DEGDM, $n=2$), tri(ethylene glycol) dimethacrylate (TEGDM, $n=3$), tetra(ethylene glycol) dimethacrylate (TtEGDM, $n=4$) and poly(ethylene glycol 400) dimethacrylate (PEGDM, $n=8.7$).



$CH_2{=}C(CH_3){-}C({=}O){-}O{-}C_{12}H_{25}$

DDM



$CH_2{=}C(CH_3){-}C({=}O){-}O{-}(CH_2CH_2O)_n{-}C({=}O){-}C(CH_3){=}CH_2$

OEGDM

2. Experimental

The monomers were purchased from Aldrich and purified by column chromatography before use. Their viscosities and the concentrations of double bonds are given in Table 1.

Reaction rate profiles and conversions were determined by isothermal differential scanning calorimetry. The DSC instrument (Unipan-Termal, Warsaw, Poland) equipped with a lid especially designed for photochemical measurements was calibrated with a standard indium sample of known mass, melting point temperature and known associated enthalpy change. Throughout the experiments the DSC unit was operated isothermally at 40 ± 0.01 °C. The 10-mg samples were

Table 1
Concentrations of double bonds and viscosities of the monomers used

Monomer	Concentration of double bonds (mol/L)	η (mPa s) at 25 °C	Literature
EGDM	10.51	6	[27]
		3.2	[28]
		6	[29]
DEGDM	8.92	5	[29]
		5	[30]
TEGDM	7.62	12.08	[28]
		10	[29]
		9	[30]
		9.4	This work
TtEGDM	6.66	14	[27]
		14	[29]
		15	[30]
PEGDM	3.97	45	[29]
DDM	3.42	6	[27]
		6	[29]
		6	[31]

polymerized in open aluminum pans having a diameter of 6.6 mm. The DSC chamber was purged with argon of high purity ($<0.0005\%$ of O_2) for 10 min prior to irradiation in order to remove oxygen from the chamber and that dissolved in the sample. The polymerization was initiated by the light of a medium pressure Hg lamp (glass filter 366 nm, light intensity 1 mW/cm^2). As the photoinitiator 2,2-dimethoxy-2-phenylacetophenone in concentration 1 wt% was used. All DSC photopolymerization experiments were conducted at least in triplicate. The reproducibility of the results was about ±3%. For computations, the heat of polymerization was taken to be 56 kJ/mol double bonds [32].

The postpolymerization processes were registered after stopping the irradiation at various degrees of double bond conversion. The reaction diffusion parameters C_{RD} were determined from the postpolymerization curves. Assuming exclusively bimolecular termination, C_{RD} can be calculated from the following equation (derived from the bimolecular termination model, equation describing the dark polymerization [33,34]):

$$\frac{1}{(R_p)_1} - \frac{1}{(R_p)_0} = 2C_{RD}(t_1 - t_0) \tag{1}$$

where R_p is the polymerization rate, t is the polymerization time, subscripts 0 and 1 denote the parameters at the moment of stopping the irradiation and after the time of the reaction in the dark, respectively. The decrease of the reaction rate over 50 s reaction time after the light was removed ($t_1 - t_0 = 50$ in Eq. (1)) was used to calculate the value of C_{RD}.

For the determination of the reactivity ratios the 10 mg samples were irradiated in the DSC chamber for a time needed to obtain $\leq 5\%$ conversion of double bonds (as estimated by DSC method) and after irradiation were immediately treated with chloroform containing small amount of hydroquinone to extract unreacted monomers. The soluble polymer was precipitated by methanol and the filtrate was analyzed for unreacted monomers by gas chromatography. In the case of ^{1}H NMR investigation, 0.5 g samples were polymerized in vials to conversions ≤ 5 wt% and the soluble copolymer was analyzed.

The reactivity ratios were estimated by the use of ProCop computer program [9,14].

3. Results and discussion

3.1. Kinetics

All the monomers used are completely miscible at all their ratios. The viscosities of DDM and OEGDM do not differ substantially (they are in the range of about 6–45 mPa s at 25 °C, Table 1), thus the main effect on the polymerization kinetics will result from the cross-linking density of the copolymer, determined by the monomer molar ratios. The rate profiles for DDM/OEGDM polymerizations at various monomer ratios are shown in Fig. 1. As could be expected, the position and the value of the maximum polymerization rate (R_p^{max}) of the system strongly depend on the cross-link density of the polymerizing system.

For systems containing OEGDM with short spacers between the methacrylate groups, at certain monovinyl/divinyl monomer ratio R_p^{max} reaches the highest value. The dependence of R_p^{max} on DDM content along with the same dependence of the final degree of double bond conversion p^f and conversion at R_p^{max} (p_{Rm}) is shown in Fig. 2. As can be seen, the composition showing the optimum balance of the accelerating and retarding effects of DDM addition changes with the length of the spacer group in OEGDM and shifts to lower DDM content with elongation of the spacer (with the decrease in cross-linking density). The p_{Rm} values increase with DDM content due to the later appearance of decelerating processes caused by lower cross-link density, but from DDM content of about 60 mol% the influence of the spacer length becomes very low.

The final degree of double bond conversion depends on the mobility of the polymer network and usually a part of pendant double bonds remains unreacted due to shielding effects. Only in the case of PEGDM the mobility of its polymer network was so high that any addition of DDM did not influence the final conversion, which was practically the same for all the compositions. The reason why the conversions of compositions containing about 90–99 mol% of DDM are somewhat higher than those of neat DDM is still not clear.

An increase in cross-linker concentration in slightly cross-linked systems causes an enhancement of the gel effect due to enhanced cross-linking resulting in slowing-down of the translational/segmental diffusion of macroradicals. This leads to a decrease of the termination rate coefficient and to an increase in the maximum polymerization rate (an additional accelerating factor is the increase in the double bond concentration because any addition of OEGDM to DDM increases the concentration of double bonds; the lowest increase occurs in the case of PEGDM (Table 1)). On the other hand, the drop of the maximum polymerization rate for DDM/EGDM mixtures when DDM content decreases from 70 to 0 mol% cannot be associated with an increase in the bimolecular termination rate coefficient, because the mobility of the radical chain ends decreases at higher cross-linker concentration. After overcoming a threshold cross-linker concentration the network becomes so dense that the termination becomes completely reaction diffusion controlled from early polymerization stages. Because the appearance of the reaction diffusion control of the termination is usually associated with reaching a degree of network density (or network immobility), it determines the degree of double bond conversion at which R_p^{max} occurs. In this way the addition of the monomethacrylate to the dimethacrylate reduces diffusional limitations and shifts the deceleration to higher conversions allowing the maximum polymerization rate to increase. When the polymer network is sufficiently mobile this factor becomes less important, as in the case of DDM/PEGDM system, where the polymerization rate decreases monotonically with DDM content in the feed.

Fig. 3 presents the dependence of the reaction diffusion parameter, C_{RD}, for several different DDM/OEGDM

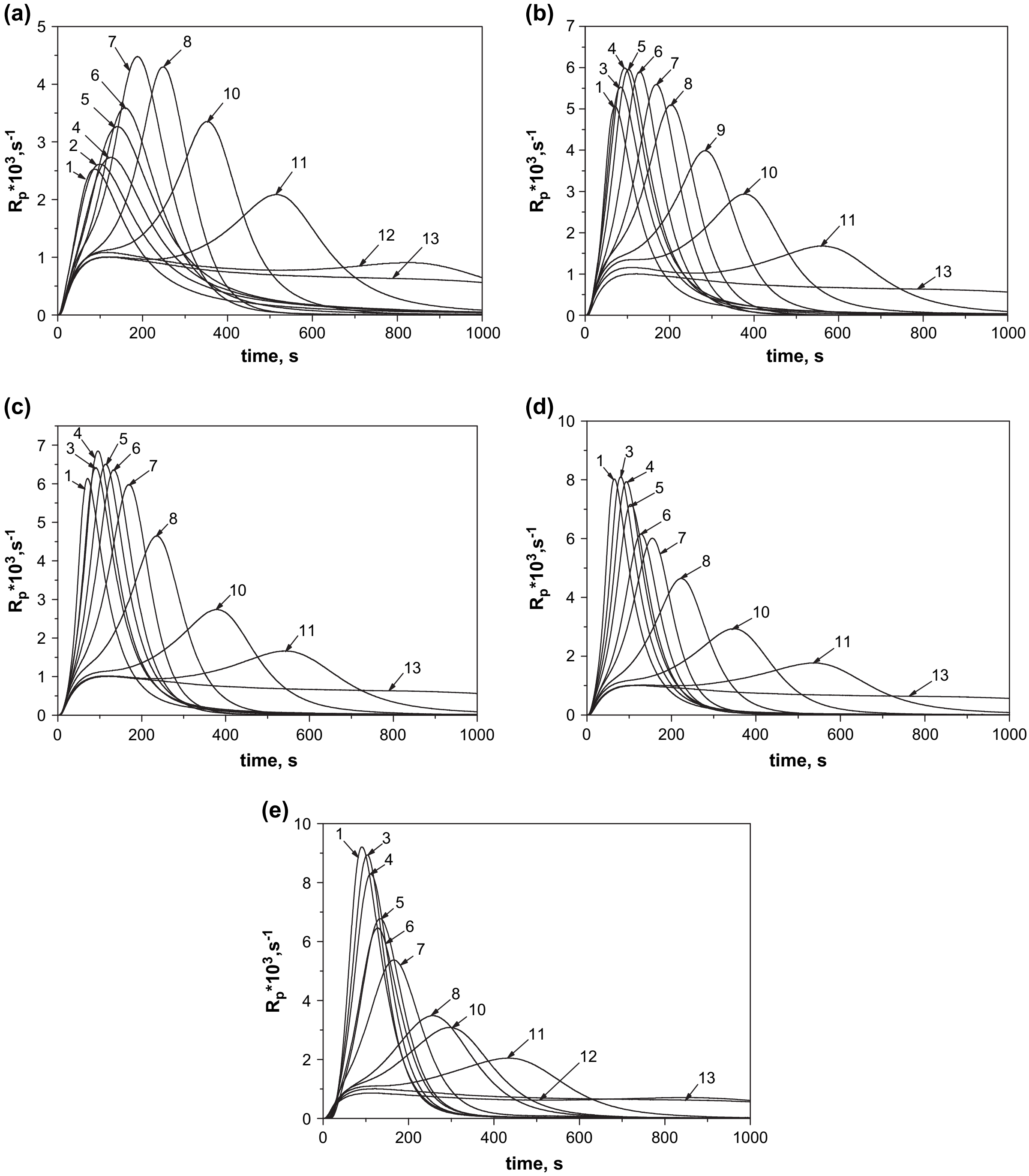


Fig. 1. Polymerization rate profiles for: (a) DDM/EGDM, (b) DDM/DEGDM, (c) DDM/TEGDM, (d) DDM/TtEGDM, and (e) DDM/PEGDM systems. The numbers 1–13 indicate the polymerization curves of systems containing 0, 20, 30, 40, 50, 60, 70, 80, 85, 90, 95, 99 and 100 mol% of DDM, respectively. Polymerization temperature: 40 °C.

compositions along with the conversion (p) dependence of the polymerization rate. C_{RD} is defined by Eq. (2) [33]:

$$k_{\mathrm{t,RD}} = C_{\mathrm{RD}} k_{\mathrm{p}}[\mathrm{M}] \tag{2}$$

where $k_{\mathrm{t,RD}}$ is the rate coefficient for termination by reaction diffusion, k_{p} is the propagation rate coefficient and [M] is the amount concentration of double bonds.

Typically C_{RD} (as calculated from Eq. (1)) decreases rapidly at the beginning of the polymerization and reaches a plateau when the reaction diffusion begins to dominate the termination [33]. In our case, for DDM/EGDM system (Fig. 3a) and DDM content 70–100 mol%, the initial rapid drop of C_{RD} slows down at about 10% of double bond conversion, but until about 60% of conversion the $C_{\mathrm{RD}} = f(p)$ plot does not reach a plateau suggesting that at these conversions the reaction diffusion does not control completely the

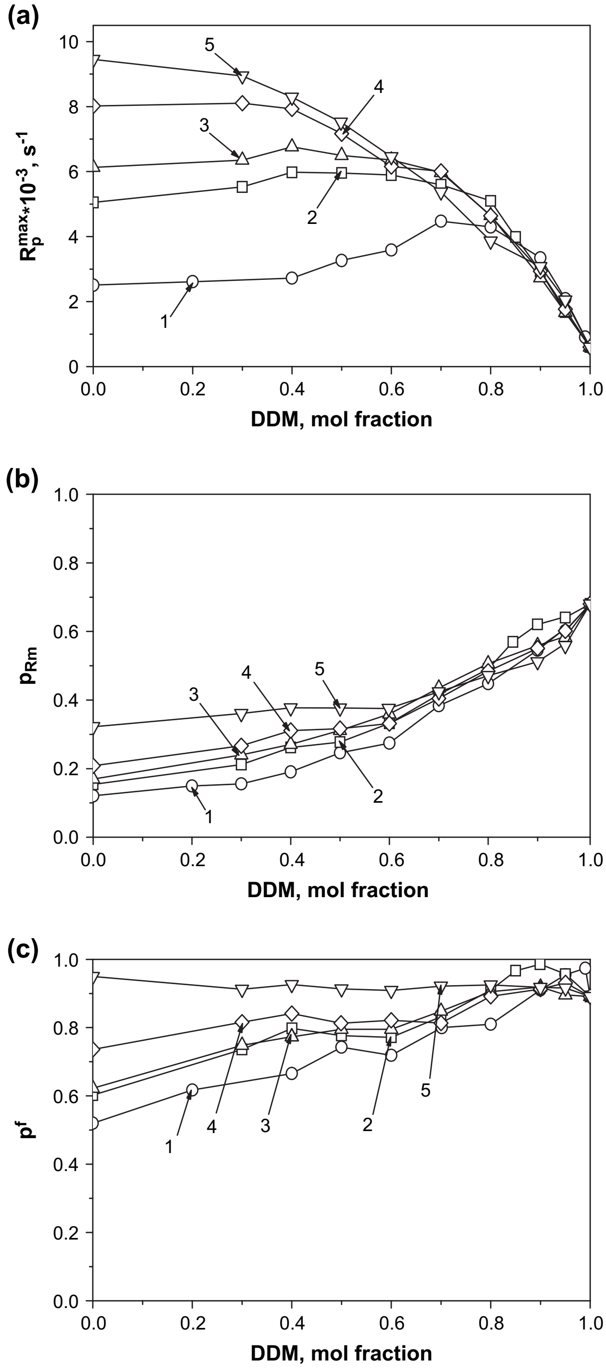


Fig. 2. Maximum polymerization rate (R_p^{max}), conversion at R_p^{max}(p_{Rm}) and final double bond conversion (p^f) as a function of DDM content in the feed: (1) DDM/EDGM, (2) DDM/DEGDM, (3) DDM/TEGDM, (4) DDM/TtEGDM, and (5) DDM/PEGDM.

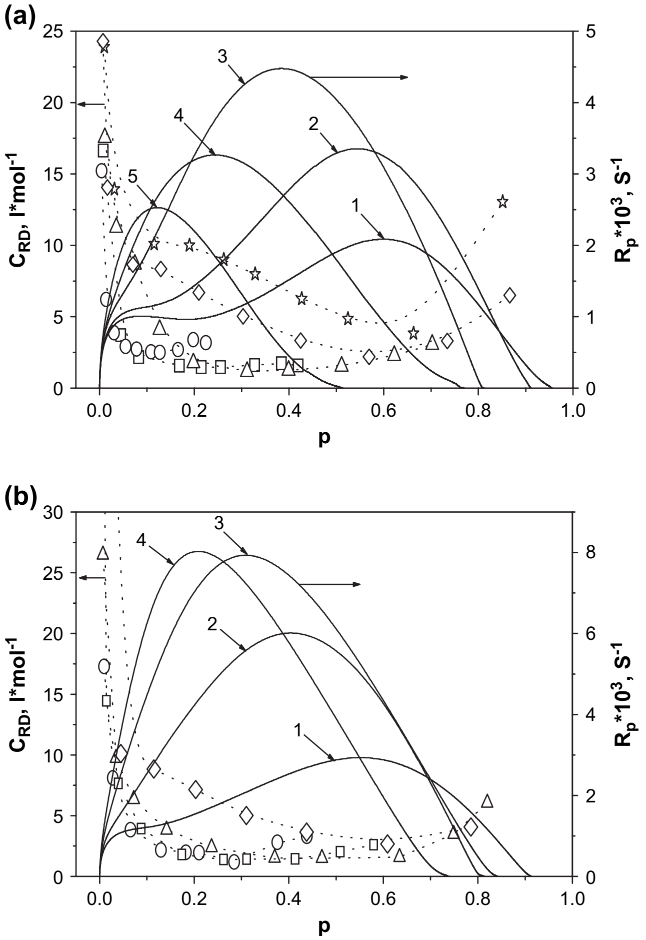


Fig. 3. The dependence of the reaction diffusion parameter C_{RD} and the polymerization rate R_p on double bond conversion p for DDM/EGDM (a) and DDM/TtEGDM (b) systems at various DDM content in the feed: (a) 1, ☆ – 95 mol%; 2, ◇ – 90 mol%; 3, △ – 70 mol%; 4, □ – 50 mol%; 5, ○ – 0 mol%; (b) 1, ◇ – 90 mol%; 2, △ – 70 mol%; 3, □ – 40 mol%; 4, ○ – 0 mol%.

termination. The C_{RD} values in the range of their slower changes are the lower, the lower DDM concentration is, indicating growing limitations in the mobility of the reacting species. For DDM content 0–70 mol%, after the initial drop C_{RD} reaches a plateau showing that from the beginning of the plateau reaction diffusion becomes the main termination mechanism. The plateaus begin at about 50% of the conversion at R_p^{max}. The plateau appears first on the $C_{RD} = f(p)$ plot corresponding to the most reactive composition (showing the highest R_p^{max} value, at DDM content 70 mol%) and C_{RD} values are the lowest. Further decrease of DDM content does not lower the plateau level suggesting that the further increase in the network density and reduction of the physical diffusion of macroradical chain ends influence the termination mechanism in a different way (see below), but shift only the transition from the translational/segmental diffusion to the reaction diffusion to lower double bond conversions. The curves presented in Fig. 3 enable to observe at which polymerization stage (a point on the kinetic curve) the change in the C_{RD} behavior occurs. A qualitatively similar situation is observed for DDM/TtEGDM system (Fig. 3b).

An additional influence on the behavior of the DDM/OEGDM polymerization can exert a decrease in efficiency of the initiation (when cross-link density and degree of conversion increase, as suggested earlier [3]) and the difference in the k_p and k_t^b (the bimolecular termination rate coefficient) values of OEGDM and DDM.

The reaction diffusion parameter was calculated from the bimolecular termination model, which does not take into account the monomolecular termination [33] (the monomolecular termination in our approach is considered as a significant slowing-down of diffusion of macroradicals, which preclude the reaction between two radical centers in the time scale registered by the experimental method used [35]). The observed increase in C_{RD} values at the highest conversions and the slightly higher C_{RD} plateau level for the neat EGDM can be associated with the substantial contribution of the monomolecular reaction to the termination process in highly cross-linked (or viscous) systems, leading to the apparent increase in the bimolecular termination rate coefficient [35–37]. Such changes in the termination mechanism cause the bimolecular reaction rate equations to fail to describe the process correctly [34].

Continuing our investigations we attempted to determine the content of unreacted pendant double bonds at various reaction stages in the copolymers formed during the photopolymerization of equimolar mixtures of DDM and OEGDM. The photopolymerization of the samples of the investigated mixtures was followed by DSC at various irradiation times giving the information about the degree of double bond conversion in the sample (p^{DSC}). This double bond conversion was the sum of the conversion reached during the illumination period and during the subsequent after-affect. After polymerization the same samples were extracted with the known amount of chloroform and the extracts were analyzed by gas chromatography, which allowed the determination of the copolymer yield (p^{ch}). This procedure was repeated for various irradiation times. The results obtained showed that there is a difference between p^{DSC} and p^{ch} values, which continuously decreases with the protraction of the irradiation time (two examples are shown in Fig. 4). This indicates that at later reaction stages, at low monomer concentration, the consumption of unreacted pendant double bonds prevailed. This observation is opposed to that made for styrene/EGDM copolymerization (for this system it was found that increasing the reaction time results in a significant increase in pendant double bond ratio [17]).

The degree of the reacted double bonds in the polymer, p^{p}, can be simply obtained from the following relation:

$$p^{p} = p^{DSC}/p^{ch} \tag{3}$$

The calculations of the p^{p} after the longest irradiation times gave the following results:

DDM/EGDM – 77%
DDM/DEGDM – 79%
DDM/TEGDM – 86%
DDM/TtEGDM – 89%

Thus, under the conditions used, in the copolymers formed from equimolar mixtures of the monomers, from 11% (for DDM/TtEGDM) to 23% (for DDM/EGDM) of double bonds remained still unreacted.

Investigation of the after-effect gave qualitatively the same results for all the DDM/OEGDM systems. The exemplary results obtained for DDM/TtEGDM polymerization as the dependence of the double bond conversion in the dark (p_D) on the degree of conversion at which the illumination has been cut off (p_L) are shown in Fig. 5. The plots obtained have the same shapes as the $R_p = f(p)$ curves, which suggest that the extent of conversion in the dark depends mainly on the concentration of the active radicals present in the system at the beginning of the after-effect (and also on the concentration of the available double bonds). Although the total radical concentration during the photopolymerization increases, a part of them becomes trapped in the network (the monomolecular termination) and the active population decreases above conversions corresponding to the maximum polymerization rate, p_{Rm} [38].

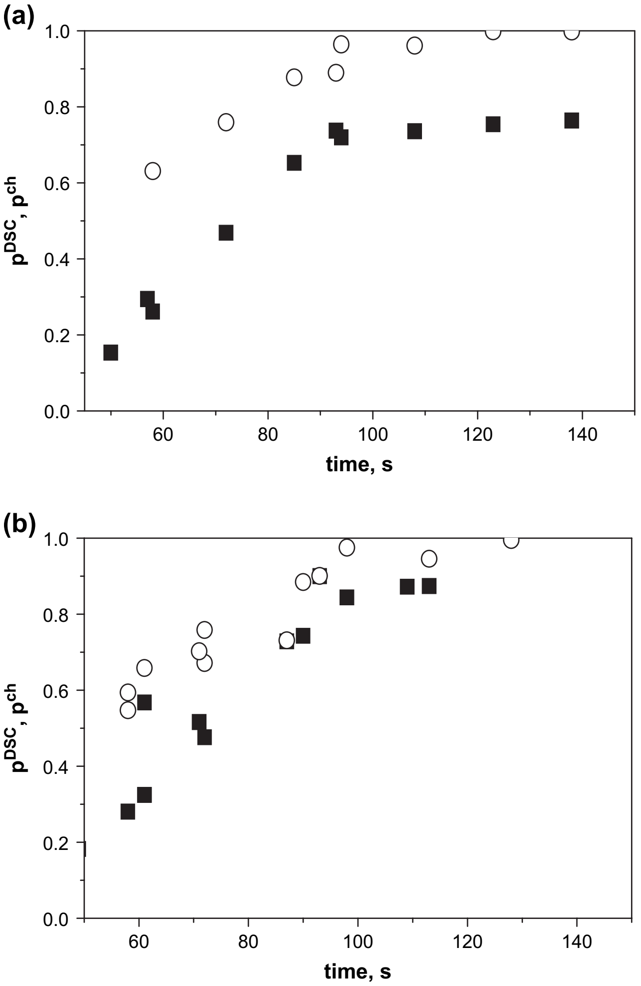


Fig. 4. The dependence of the polymer yield p^{ch} (open symbols) and double bond conversion p^{DSC} (filled symbols) on irradiation time for the photoinitiated polymerization of equimolar mixtures of (a) DDM and DEGDM and (b) DDM and TtEGDM.

The dark conversion can be high and can significantly exceed that reached before discontinuation of the irradiation. The higher the cross-linker concentration in the feed, the higher the conversion in the dark (for conversions p_L lower than conversions p_{Rm}). This dependence results from the suppression of the termination reaction in cross-linked systems. The mutual dependence of p_D and p_L can be better expressed by the p_D/p_L ratio plotted as a function of p_L (Fig. 6). The p_D/p_L ratio can also be considered as the efficiency of the dark reaction. Being very

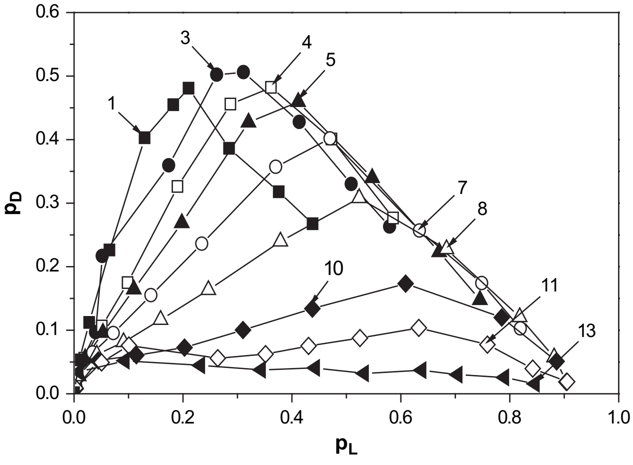


Fig. 5. The dependence of the conversion in the dark (p_D) on the conversion at which the irradiation has been interrupted (p_L) for DDM/TtEGDM polymerization. Description of the curves as in Fig. 1.

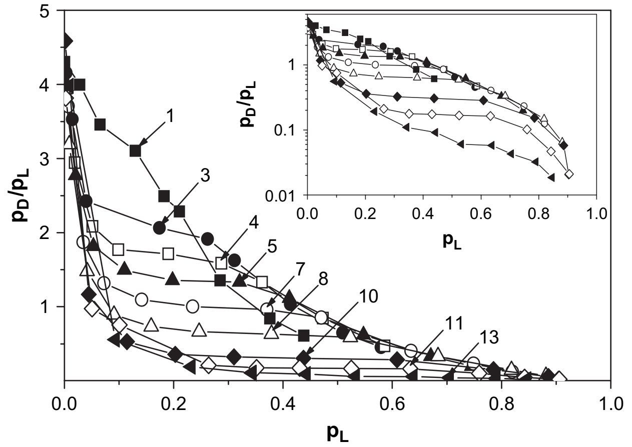


Fig. 6. The dependence of the p_D/p_L ratio on the conversion at which the irradiation has been interrupted (p_L) for DDM/TtEGDM polymerization. Description of the curves as in Fig. 1.

high at the beginning of the polymerization, it decreases rapidly and then reaches a plateau in a range of conversions ending close to p_{Rm}. This means that in this conversion range p_D is practically proportional to p_L. The beginning of the plateau corresponds to the beginning of the dominance of the reaction diffusion as the termination mechanism. A qualitatively similar dependence can be obtained by plotting $R_p/p = f(p)$; this gives an interesting result: at the plateau range of $R_p/p = f(p)$ function the curve $R_p = f(p)$ is roughly a straight line. However, this phenomenon can be observed only for relatively slightly cross-linked systems.

For highly cross-linked systems the total conversion $p^{tot}(p^{tot} = p^{DSC})$, the sum of the conversion reached during the illumination period (p_L) and during the after-affect (p_D), increases strongly with p_L until p_L reaches p_{Rm}. Further illumination results only in a slight conversion increase (Fig. 7). On the other hand, for linear and slightly cross-linked systems, p^{tot} is almost proportional to p_L. This result can be helpful in the determination of the illumination times for practical applications.

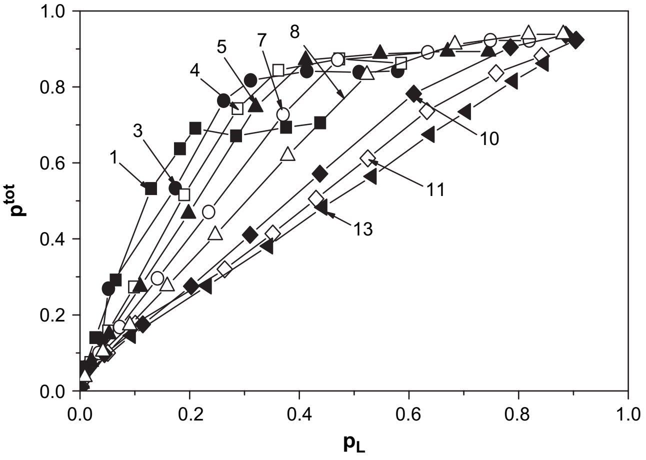


Fig. 7. The dependence of the total conversion p^{tot} on the conversion at which the irradiation has been interrupted (p_L) for DDM/TtEGDM polymerization. Description of the curves as in Fig. 1.

3.2. Reactivity ratios

Determination of reactivity ratios for monovinyl/divinyl systems meets many experimental difficulties associated mainly with the analysis of the resulting cross-linked polymer. Thus, when using the popular methods of analysis, one needs to analyze either the unreacted monomers or soluble copolymer obtained at very low conversions and at low divinyl monomer

Table 2
Reactivity ratios for dodecyl methacrylate (DDM) and ethylene glycol dimethacrylates (OEGDM) determined by various calculation methods

Composition	Calculation method	r_1 (DDM)	r_2 (OEGDM)	Standard deviation
DDM/EGDM	KT	0.225	1.534	0.076
	YBR	0.238	1.281	0.077
	TM	0.338	2.017	0.074
	OPT	0.322	2.029	0.070
	PTM	$r_{11} = 0.400$	$r_{22} = 1.731$	0.068
		$r_{21} = 0.299$	$r_{12} = 3.961$	
DDM/DEGDM	KT	0.472	1.023	0.021
	YBR	0.430	1.023	0.021
	TM	0.425	0.920	0.020
	OPT	0.415	0.918	0.018
	PTM	$r_{11} = 0.132$	$r_{22} = 1.671$	0.014
		$r_{21} = 0.465$	$r_{12} = 0.336$	
DDM/TEGDM	KT	0.317	1.886	0.056
	YBR	0.223	1.698	0.058
	TM	0.298	1.613	0.053
	OPT	0.288	1.631	0.034
	PTM	$r_{11} = 0.058$	$r_{22} = 4.203$	0.042
		$r_{21} = 0.409$	$r_{12} = 0.347$	
DDM/TtEGDM	KT	0.350	1.264	0.091
	YBR	0.339	1.241	0.090
	TM	0.332	1.276	0.090
	OPT	0.321	1.087	0.089
	PTM	$r_{11} = 7.670$	$r_{22} = 58.137$	0.068
		$r_{21} = 0.005$	$r_{12} = 0.009$	

TM – Tidwell–Mortimer, YBR – Yezrielev–Brokhina–Roskin, OPT – optimization, KT – Kelen–Tüdos, PTM – the method taking into account the penultimate effect.

content. These factors increase the experimental error. In this work the copolymer composition was determined by gas chromatography analysis of the unreacted monomers at higher OEGDM concentrations and by ^{1}H NMR analysis of soluble copolymers formed at low OEGDM content in the feed.

The reactivity ratios were calculated for four monomer pairs: DDM/EGDM, DDM/DEGDM, DDM/TEGDM and DDM/TtEGDM using the convention in which the divinyl monomer is treated the same as the one–double-bond monomer. Several calculation methods, both linear and non-linear, were used: Kelen–Tüdos (KT, linear), Yezrielev–Brokhina–Roskin (YBR, linear), Tidwell–Mortimer (TM, non-linear), optimization (OPT, non-linear), all of them based on the terminal model, and a method taking into account the penultimate effect (PTM). The calculated monomer reactivity ratios are given in Table 2.

In almost all the cases (one exception: r_2 close to 1 for DDM/DEGDM system) the r_2 values are higher than 1 and r_1 values are lower than 1 suggesting a higher activity of the divinyl monomers in addition to the copolymer chain. This in turn indicates that the polymer formed at the beginning of the reaction will be more densely cross-linked than that formed in the final reaction stages.

The detailed analysis of the results obtained from the PTM method is out of the scope of this work. However, it can be easily observed that the effect of the next-to-last unit on the reactivity of the growing free radical increases with the length of the dimethacrylate monomer, because the differences between r_{11} and r_{21} as well as between r_{22} and r_{12} increase. (When $r_{11}=r_{21}$ and $r_{22}=r_{12}$ the PTM model reduces to the terminal model.) The penultimate unit may affect the radical reactivity both by electronic and steric effects [14].

The composition diagrams for DDM/DEGDM and DDM/TEGDM systems are presented in Fig. 8. Points correspond to experimentally determined copolymer compositions. Theoretical curves were calculated according to the above mentioned calculation methods. As can be seen, there is a good agreement between the experimental data and the theoretical curves (despite a scatter of data in Fig. 8a).

It is difficult to state univocally, which calculation method is the best for a given system. It was suggested that the best criterion for choosing the calculation method is the best fitting of the theoretical curve obtained from the calculated reactivity ratios to the experimental points and that in many cases both the linear as well as the non-linear methods give the correct results [14].

The monomers investigated in this work were two- and tetrafunctional in pairs. According to second convention in kinetic models for copolymerization, when we define the difunctional monomer (DDM) as M_1 and OEGDM as M_2,

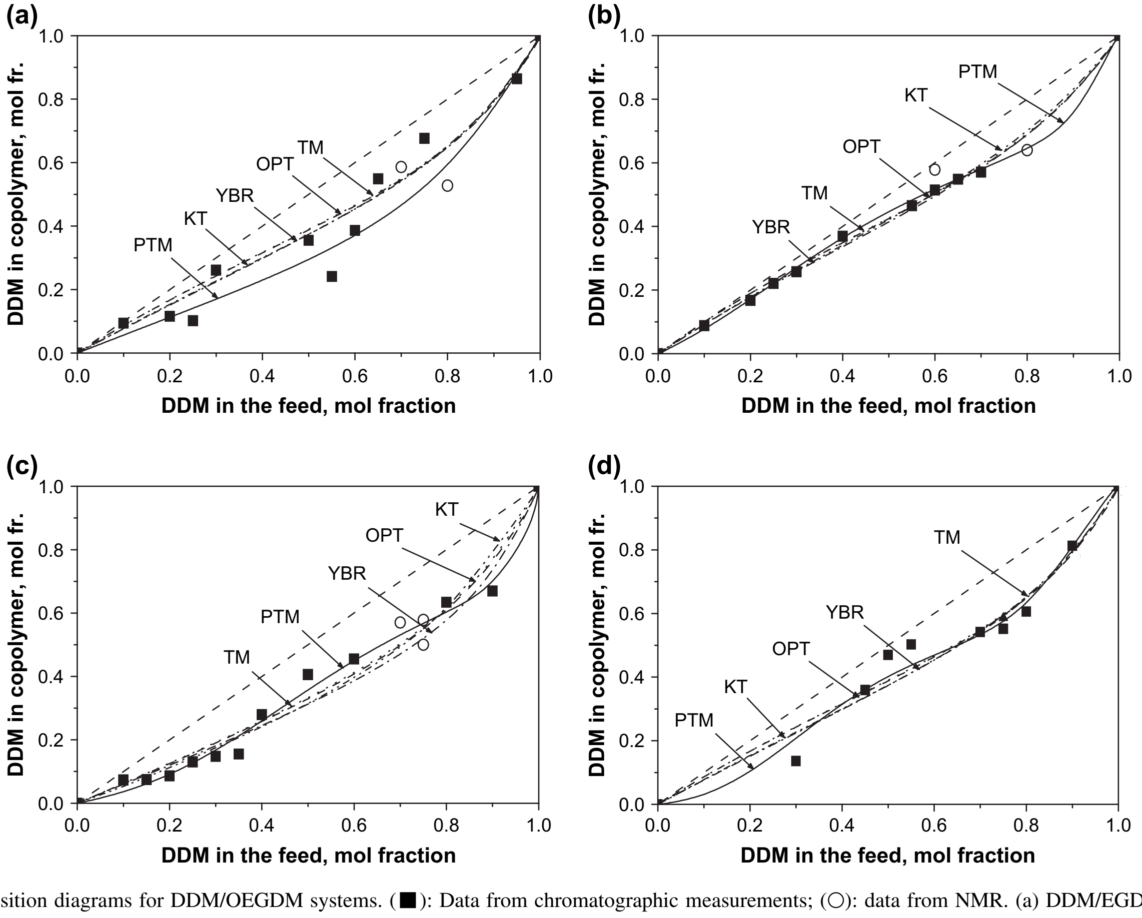


Fig. 8. Composition diagrams for DDM/OEGDM systems. (■): Data from chromatographic measurements; (○): data from NMR. (a) DDM/EGDM, (b) DDM/DEGDM, (c) DDM/TEGDM, and (d) DDM/TtEGDM. Calculation methods: TM – Tidwell–Mortimer, YBR – Yezrielev–Brokhina–Roskin, OPT – optimization, KT – Kelen–Tüdos, and PTM – the method taking into account the penultimate effect.

we obtain that in the classical copolymerization equation the reactivity ratios will be defined as:

$$r_1' = \frac{k_{11}}{2k_{12}} \tag{4}$$

$$r_2' = \frac{2k_{22}}{k_{21}} \tag{5}$$

In the case, when the polymerizing group is the methacrylate function, theoretically the homopropagation (k_{11} and k_{22}) and co-propagation (k_{12} and k_{21}) rate constants should be the same. In such a case $r_1' = 0.5$ and $r_2' = 2$.

In reality the propagation rate constants are different for different methacrylates [39]. Moreover, as mentioned earlier, the reactivity ratios in methacrylate/methacrylate systems, theoretically equal to 1, differ from 1 in majority of cases. The observed deviations of the calculated reactivity ratios presented in Table 2 from the theoretical values (0.5 and 2) may result from several factors, like different homopropagation and co-propagation rate constants, difference in the diffusion coefficients of the comonomers in the viscous reaction medium when the autoacceleration begins at the very early stages of the polymerization, difference in the reactivity of the monomeric and pendant double bonds, steric factors, occurrence of cyclization, etc.

Although the reactivity ratios were determined for several monovinyl/divinyl systems (methacrylate/dimethacrylate [11,18], styrene/dimethacrylate [17,20,22], styrene/divinylbenzene [22]), the functionality of the comonomers was seldom discussed. According to Eq. (4) the reactivity ratio r_1' of the radical centered on DDM *mer* with the first double bond of the diester is twice of the calculated r_1 value. Thus, the r_1' values can be obtained by multiplying the r_1 values from Table 2 by factor of 2. So-obtained reactivity ratios are still in each case lower than 1 indicating that even when the differences in functionalities of the monomers are taken into account, the DDM radical preferentially reacts with the diester than with its own monomer.

From the integral form of the copolymerization equation [14] we can obtain the variation of the instantaneous composition of the comonomer mixture (M), the instantaneous copolymer composition (m), and the overall copolymer composition (om) at each moment of the copolymerization process. The theoretical curves obtained from the reactivity ratios calculated by Tidwell–Mortimer method for the equimolar mixtures of the comonomers are given in Fig. 9 along with the

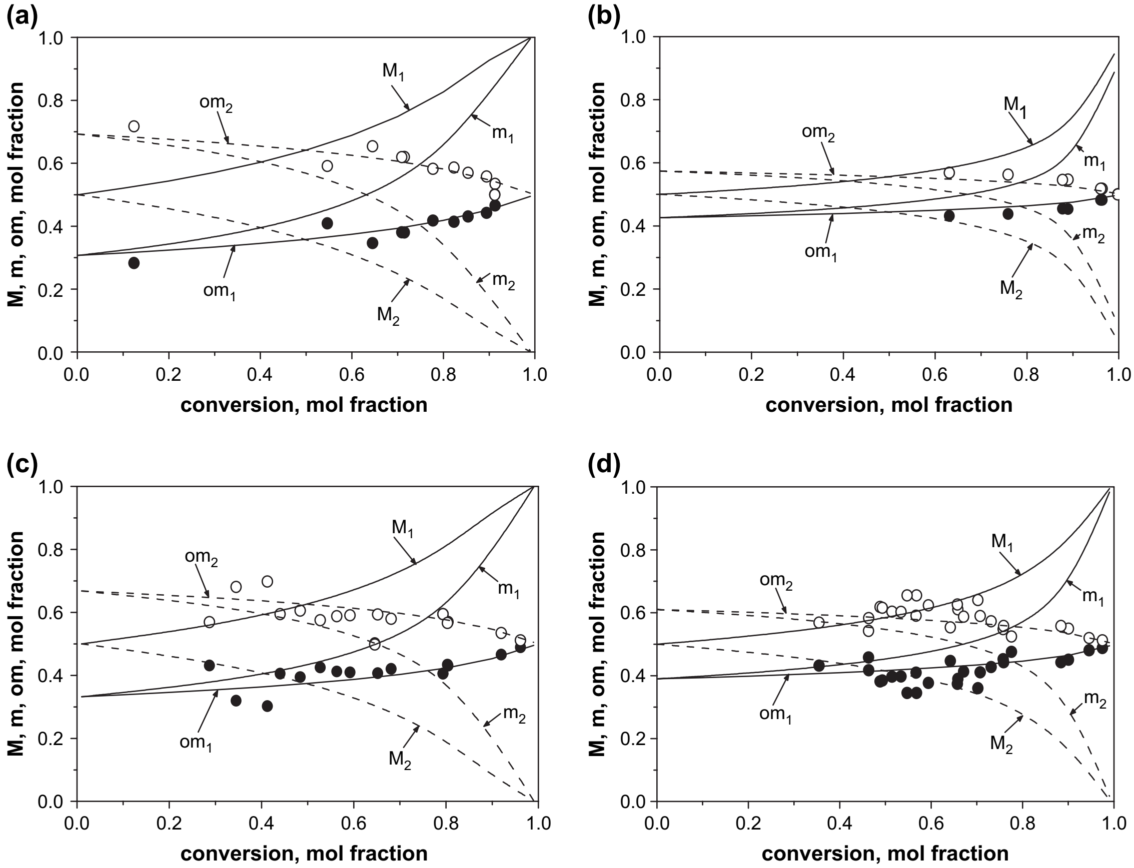


Fig. 9. Dependence of the instantaneous composition of the comonomer mixture (M), of the instantaneous copolymer composition (m) and the overall copolymer composition (om) on the polymer yield for the copolymerization of equimolar mixtures of DDM (subscript 1, filled symbols) and OEGDM (subscript 2, open symbols). Curves calculated using the reactivity ratios obtained by Tidwell–Mortimer method (Table 2). Points represent experimental data. (a) DDM/EGDM, (b) DDM/DEGDM, (c) DDM/TEGDM, (d) DDM/TtEGDM.

points representing the experimental data. The conversions correspond to the polymer yield (from GC measurements).

The difference between the molar fraction of the comonomers chosen for the startup of the copolymerization and that in the copolymer is the lowest for DDM/DEGDM mixture, however, all the curves presented in Fig. 9 show the preferential addition of DDM to the growing free radical. Throughout the copolymerization process the molar fraction of DDM within the monomer mixture exceeds the value of the molar fraction of the same comonomer in the copolymer. The global copolymer represents a copolymer of high compositional heterogeneity, but which finally recovers (at 100% conversion) the composition of the initial comonomer mixture. The dependence of the overall copolymer composition on the copolymer yield determined on the basis of the reactivity ratios calculated from the experimental data obtained at very low conversions is in good agreement with the experimental data obtained for higher copolymer yields and points to the accuracy of the determination of the reactivity ratios.

4. Conclusions

For systems containing OEGDM with short spacers between the methacrylate groups, at certain monovinyl/divinyl monomer ratio, R_p^{max} reaches the highest value. The main factor, which controls the appearance of the most reactive composition for low viscosity comonomers is the cross-link density of the resulting copolymer. For low cross-linker concentrations the $C_{RD} = f(p)$ plots do not reach a plateau at the whole conversion range investigated suggesting that the reaction diffusion does not control completely the termination. After overcoming a threshold cross-linker concentration the network becomes so dense that the termination becomes completely reaction diffusion controlled from early polymerization stages. This is reflected by the formation of a plateau on the $C_{RD} = f(p)$ plot. The plateaus are formed on the $C_{RD} = f(p)$ plots for all the monomer ratios, for which the increase in OEGDM content decreases the maximum polymerization rate. The plateau appears first on the $C_{RD} = f(p)$ plot corresponding to the most reactive composition (showing the highest R_p^{max} value, in DDM/EGDM mixture at DDM content 70 mol%) and C_{RD} values are the lowest.

Determination of the content of unreacted pendant double bonds at various reaction stages in the copolymers formed during the photopolymerization of equimolar mixtures of DDM and OEGDM showed that at the late reaction stages, at low monomer concentration, the consumption of unreacted pendant double bonds prevails. At the end of the reaction, still from 11% (for DDM/TtEGDM) till 23% (for DDM/EGDM) of double bonds remains unreacted.

The dark conversion can be high and can significantly exceed that reached before discontinuation of the irradiation. The higher the cross-linker concentration in the feed, the higher the conversion in the dark (for conversions p_L lower than conversions p_{Rm}). For relatively slightly cross-linked systems the p_D/p_L ratio plotted as a function of p_L reaches a plateau which begins at conversions corresponding those at which the reaction diffusion begins to dominate the termination mechanism.

Determination of the reactivity ratios by five calculation methods using the convention in which the divinyl monomer is treated the same as the one–double-bond monomer showed that r_1 (DDM) values were lower than 1 and the r_2 (OEGDM) values were higher than 1 indicating that the polymer formed at the beginning of the reaction is more densely cross-linked than that formed in the final reaction stages. When the second convention, which takes into account the differences in functionalities of the monomers was considered, the so-obtained reactivity ratios for DDM were again in each case lower than 1 indicating that the DDM radical preferentially reacts with the diester than with its own monomer.

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