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Photopolymerization of Di- and Tetrafunctional Methacrylic Monomers in a Polymeric Medium: Kinetics and Evidence of Reaction Diffusion Throughout the Photopolymerization Reaction

J. L. Mateo,* J. Serrano, and P. Bosch

Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

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ABSTRACT: The photopolymerization behavior and reaction kinetics of ethylhexyl methacrylate (EHMA) and ethylene glycol dimethacrylate (EGDMA) monomers in styrene−butadiene−styrene block copolymer (SBS) were studied. For both monomers, di- and tetrafunctional, reaction diffusion was found to be the only mechanism of termination when the polymerization is carried out in this polymeric medium, that is, reaction diffusion controls the termination reaction from the beginning of the reaction. The polymerization of EGDMA in polystyrene and polybutadiene showed similar behavior to that in SBS. Also, the relationship between the individual rate constants k_t and k_p was studied, and a constant ratio of these kinetic constants was found.

Introduction

The photoinduced polymerization and photo-cross-linking of acrylic monomers have become increasingly important in recent years due to the large number of possible applications of this technology. Some of these applications take place in fields such as microelectronics,[1] surface improvements,[2] and information recording.[3] For many of these applications, principally those linked with the image formation, a polymeric binder is required because the starting material needs to be a clear, transparent, and nontacky film or sheet and also because the properties of the binder are many times determinant as for the end use of the photopolymer.

It can be assumed that the polymerization reactions of acrylic monomers in a polymeric medium take place in the diffusion-limited region, and therefore, the formed macroradicals must exhibit a minimum of mobility in the polymer system.[4] In these cases reaction diffusion must be considered in addition to the diffusion-controlled termination mechanism. Reaction diffusion occurs when the "frozen" polymer radical propagates through the matrix of unreacted functional groups until encountering a second active chain radical and terminating. Therefore, the mechanism of the polymerization reaction can be assessed by following the changes of the individual kinetic constants for propagation and termination as a function of reaction conversion. Reaction diffusion has been observed at high conversions in the polymerization of methacrylic monomers[5−7] and at low conversions,[8] below 10%, in the polymerization of multifunctional acrylic monomers.

The aim of the present article is to investigate the kinetics of the photopolymerization of di- and tetrafunctional methacrylic monomers in polymeric media in order to, fundamentally, know the mechanism of the polymerization reaction and the importance of the reaction diffusion through the determination of the individual kinetic constants, k_t and k_p, comparing the obtained results with those found in bulk and in solution photopolymerization of methacrylic monomers.

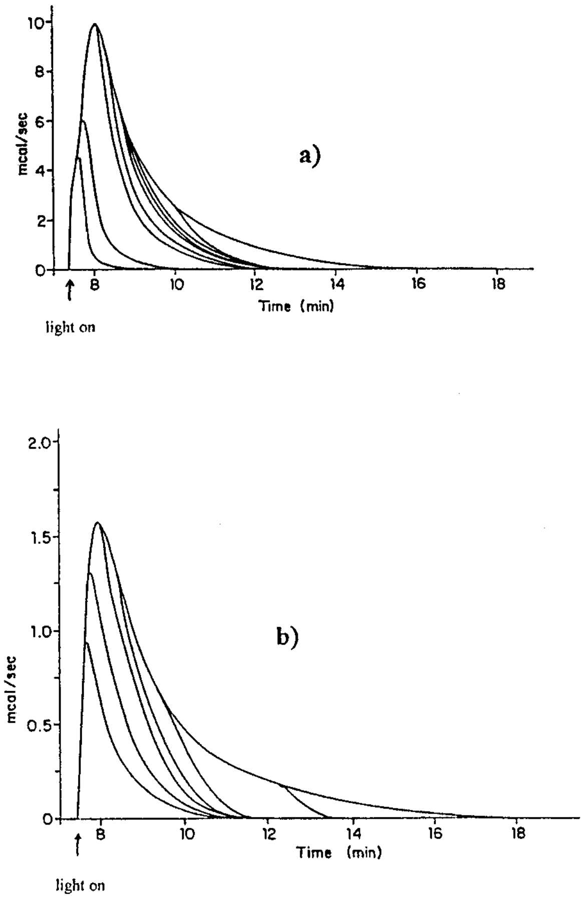

Figure 1. (a) Rate of polymerization as a function of time for eight different dark reactions during the bulk photopolymerization of EGDMA with 1% DMPA at 40 °C and 3.47×10^{-5} einstein·L^{-1}·s^{-1} of absorbed intensity at 365 nm. (b) Rate of polymerization as a function of time for six different dark reactions during the photopolymerization of EGDMA in SBS block copolymer with 1% DMPA at 40 °C and 2.63×10^{-5} einstein·L^{-1}·s^{-1} of absorbed intensity at 365 nm. Monomer concentration: 0.66 mol·L^{-1}.

Experimental Section

Materials. Butyl methacrylate (BMA), ethylhexyl methacrylate (EHMA) and ethylene glycol dimethacrylate (EGD-

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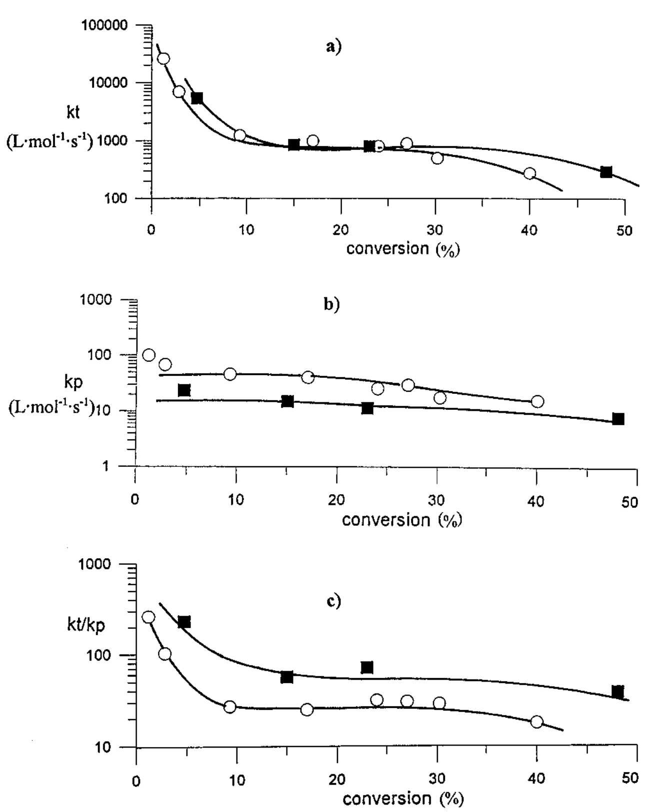

Figure 2. (a) Termination kinetic constant, k_t, as a function of double-bond conversion for bulk photopolymerization of EGDMA (○) and ethyl benzoate solution (■). (b) Propagation kinetic constant, k_p, as a function of double-bond conversion for photopolymerization of EGDMA in bulk (○) and ethyl benzoate solution (■). (c) Ratio of k_t/k_p as a function of double-bond conversion for photopolymerization of EGDMA in bulk (○) and ethyl benzoate solution (■). Experimental conditions: for bulk photopolymerization, 1% DMPA, 40 °C, $I_a = 3.47 \times 10^{-5}$ einstein·L^{-1}·s^{-1}; for ethyl benzoate solution photopolymerization, 1% DMPA, 40 °C, $I_a = 2.46 \times 10^{-4}$ einstein·L^{-1}·s^{-1}, monomer concentration = 0.65 mol·L^{-1}.

MA) monomers from Aldrich (98%) were used without further purification. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) photoinitiator from Ciba Geigy was used as received. Ethyl benzoate (99%) from Merck was used as solvent without further purification.

Styrene−butadiene−styrene block copolymer denoted as C-501 (REPSOL S.A.) of M_n = 100 000 and M_w = 110 000, containing 31% polystyrene (100% block) and 69% polybutadiene, with 50% of the polybutadiene fraction as 1,4-cis, 40% as 1,4-trans, and 10% as 1,2-isomer, was purified by precipitation with methanol from chloroform solution. Polystyrene from BASF and polybutadiene from Shell (96.5% 1,4-cis) were purified by precipitation on methanol from benzene solution.

Procedure. The photopolymerization study by differential scanning photocalorimetry (photo-DSC) was performed as described previously.[9] All the irradiations were done at 40 °C under a nitrogen atmosphere. The samples were irradiated with a Hanovia medium pressure mercury lamp, using an interference filter with a transmission maximum of 365 nm (International Light NB-365).

Cylindrical specimens of 0.56 cm diameter were cut from films of approximately 0.1 cm thick cast from a 20% toluene solution of the polymer−monomer−photoinitiator system in Petri dishes. Monomer concentrations were 12−13% (g/100 cc), and a photoinitiator (DMPA) of 1% was used in all of the photopolymerizations carried out in polymeric medium. When the polymerizations were carried out in solution or in bulk, sample quantities of 20 μL were accurately measured using a Hamilton 25 μL syringe.

Kinetic Constants Calculation. The photopolymerization rate was measured by differential scanning photocalorimetry which monitors the heat flux produced in the polymerization reaction as a function of reaction time. For this study, the heat of reaction of the methacrylate double bond used in calculations was 13.1 kcal/mol.[8] The mixture (polymer−monomer−photoiniatiator) is homogeneous and transparent, and no physical changes were observed after the photopolymerization reaction. DSC thermograms of SBS and PS specimens showed the slope change at 80−90 °C, corresponding to the T_g of the polystyrene; the transition disappeared in the thermogram of the polymer−monomer−photoinitiator system and remained without any change after the photopolymerization reaction took place.

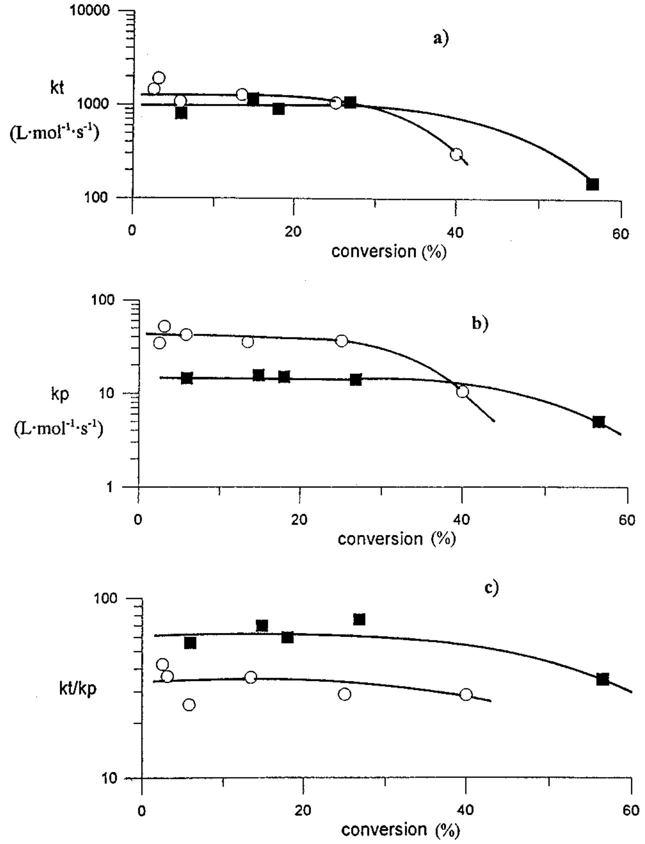

Figure 3. (a) Termination kinetic constant, k_t, as a function of double-bond conversion for photopolymerizations of EGDMA (○) and EHMA (■) in SBS block copolymer. (b) Propagation kinetic constant, k_p, as a function of double-bond conversion for the photopolymerizations of EGDMA (○) and EHMA (■) in SBS block copolymer. (c) Ratio of k_t/k_p as a function of the double-bond conversion for the photopolymerizations of EGDMA (○) and EHMA (■) in SBS block copolymer. Experimental conditions: for EGDMA photopolymerization, 1% DMPA, 40 °C, $I_a = 2.63 \times 10^{-5}$ einstein·L^{-1}·s^{-1}, monomer concentration = 0.66 mol·L^{-1}; for EHMA photopolymerization, 1% DMPA, 40 °C, $I_a = 1.25 \times 10^{-4}$ einstein·L^{-1}·s^{-1}, monomer concentration = 0.62 mol·L^{-1}.

To determine the individual kinetic constants for propagation and termination, photopolymerizations offer the unique advantage of controlling the radical generation by exposing or shielding the sample from the light source.[8,10] Once the shutter for the light source is closed, the radical balance reduces to:

$$d[M^\bullet]/dt = -2k_t[M^\bullet]^2$$

Integrating, assuming k_t is approximately constant over a small time interval, which is in fact correct in the particular case of the acrylic polymerization in a polymeric medium as it can be proved according to the obtained results in this work, and substituting the radical concentration in terms of the rate of polymerization, monomer concentration, and propagation kinetic constant ($R_p = k_p$ [M][M•]), the equation becomes the

Table 1. Photopolymerization of EGDMA (0.66 mol·L^{-1}) and EHMA (0.62 mol·L^{-1}) in SBS Block Copolymer

monomer	I_a (einstein·L^{-1}·s^{-1})	double-bond conversion (%) at R_{pmax}	R_{pmax} (mol·L^{-1}·s^{-1})	overall double-bond conversion (%)
EGDMA	2.63×10^{-5}	4.2	3.94×10^{-3}	51
EGDMA	11.1×10^{-5}	6.2	8.35×10^{-3}	64
EGDMA	25.6×10^{-5}	7.1	11.40×10^{-3}	68
EHMA	12.5×10^{-5}	5.9	3.55×10^{-3}	>95

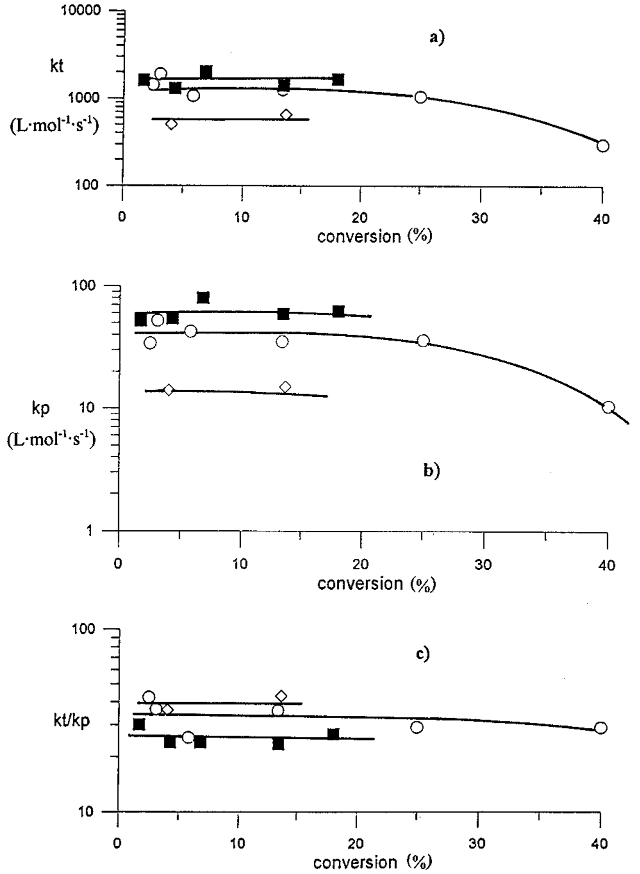

Figure 4. (a) Termination kinetic constant, k_t, as a function of double-bond conversion for the photopolymerization of EGDMA in SBS (○), PS (■), and PB (◇). (b) Propagation kinetic constant, k_p, as a function of double-bond conversion for the photopolymerization of EGDMA in SBS (○), PS (■), and PB (◇). (c) Ratio of k_t/k_p as a function of double-bond conversion for the photopolymerization of EGDM in SBS (○), PS (■), and PB (◇). Experimental conditions: for photopolymerization in SBS, 1% DMPA, 40 °C, $I_a = 2.63 \times 10^{-5}$ einstein·L^{-1}·s^{-1}, monomer concentration = 0.66 mol·L^{-1}; for photopolymerization in PS, 1% DMPA, 40 °C, $I_a = 4.42 \times 10^{-5}$ einstein·L^{-1}·s^{-1}, monomer concentration = 0.62 mol·L^{-1}; for photopolymerization in PB, 1% DMPA, 40 °C, $I_a = 1.05 \times 10^{-4}$ einstein·L^{-1}·s^{-1}, monomer concentration = 0.60 mol·L^{-1}.

following:

$$\frac{2(t_t - t_0)}{k_p/k_t^{1/2}} = \frac{1}{k_t^{1/2}}\left(\frac{[\mathrm{M}]_t}{R_{p(t)}} - \frac{[\mathrm{M}]_0}{R_{p(0)}}\right)$$

The subscripts 0 and t (referring to time) on the time, monomer concentration, and polymerization rate (t, M, and R, respectively) correspond to the beginning of the dark period and some time later in the dark reaction. At various time intervals, the shutter was closed, and the observed decrease in the rate of polymerization was monitored. Figure 1 shows dark reactions corresponding to bulk photopolymerizations of ethylene glycol dimethacrylate and photopolymerizations of the same monomer in a polymeric medium (styrene–butadiene–styrene block copolymer) from which the individual kinetic constants at different reaction times and double-bond conversions have been determined. For tetrafunctional monomers, it should be noted that the values of k_t and k_p are average values for the monomeric and pendant double bond.

Monomer conversion was determined from the value of conversion (heat of reaction released at a given time divided by the theoretical enthalpy: $\Delta H_t/H_{theor}n$, n being the number of double bonds present in the monomer). $R_{p(t)}$ corresponds with the rate of polymerization at time t, measured as the height of the exothermic curve at that time. $k_p/k_t^{1/2}$ was calculated from the general kinetic equation:

$$R_p = k_p/k_t^{1/2}[\mathrm{M}]I_a^{1/2}\phi_i^{1/2}$$

where I_a is the absorbed intensity by the photoinitiator taking into account that the sample in the aluminum pan receives an ultraviolet dose from the initial incident beam and a second dose from the reflected beam (the reflectance of the aluminum is 0.9642).[11] Since no data exist for the initiation efficiency (ϕ_i) of 2,2-dimethoxy-2-phenylacetophenone in these conditions, a bulk photopolymerization of butyl methacrylate was carried out using a photoinitiator concentration of 1% and taking the $k_p/k_t^{1/2}$ value of 0.16 L$^{1/2}$·mol$^{-1/2}$·s$^{-1/2}$ from the literature.[12] Taking the maximum rate of polymerization (maximum height of the exotherm, which experimentally was reached at 9 s), a value of 0.7 was found for ϕ_i, which is the value used in all of the photopolymerizations carried out with the methacrylates used in this work ($R_p = 4.89 \times 10^{-3}$ mol·L^{-1}·s^{-1}, $I_a = 3.45 \times 10^{-5}$ einstein·L^{-1}·s^{-1}).

Results

Parts a–c of Figure 2 contain the experimentally determined values for the termination and propagation kinetic constants (k_t and k_p) and the ratio k_t/k_p, respectively, in the bulk and solution photopolymerizations of EGDMA. The results are very similar to those found for bulk polymerization of multi(meth)acrylic monomers by Anseth et al.[7] The curve of k_t versus conversion showed a decrease as the diffusion of the macroradical chains became limited, reaching a constant value from about 10% of double-bond conversion until 30% of conversion. The curve of k_p versus conversion remains fairly constant, and it decreases very slowly, until a higher conversion is reached where diffusion of the monomer is significantly decreased. The decrease of the termination rate constant while propagation remains unhindered leads to the autoaccelerative behavior of this system, as can be observed in the upward part of the curve of Figure 1a. As the system approached the gel point and the maximum in its polymerization, a change in the termination mechanism was observed as denoted by the constant value of k_t until relatively high values of the double-bond conversion. Termination was no longer predominantly controlled by the segmental diffusion of the macroradicals but rather by reaction diffusion, and k_t was proportional to k_p (as seen in Figure 2c). The photopolymerization of EGDMA in ethyl benzoate solution behaves in a similar way as the bulk photopolymerization (as seen in Figure 2).

The experimental values obtained for k_t, k_p, and k_t/k_p as a function of double-bond conversion corresponding to the photopolymerizations of EGDMA and EHMA in SBS block copolymer are shown in Figure 3. Independently of the monomer functionality, di- or tetrafunctional, reaction diffusion seems to be the only mechanism of termination, given that the k_t value remains constant from the onset of the polymerization until high double-bond conversions, the constant value of k_t being similar to that found for k_t in the bulk photopolymerization of EGDMA during the step of the reaction diffusion mentioned above. The k_p and k_t/k_p values practically remain constant until high conversions, observing that k_t and k_p values corresponding to the photopolymerization of EHMA remain constant until greater conversion as compared to those in the photopolymerization of EGDMA due to a slower decreasing of the monomer diffusion in a non-cross-linked system. As a consequence of that, the overall double-bond conversion for the tetrafunctional monomer is lower than that corresponding to the difunctional monomer, as can be seen in Table 1, where data related to the maximum photopolymerization rate and to the overall double-bond conversion of the EGDMA photopolymerization in SBS block copolymer when different light intensities are used are also included. Higher polymerization rates create excess free volume in these cross-linked systems,[1] and therefore, k_t should decrease more slowly giving rise to higher overall double-bond conversion (as shown in Table 1). From Table 1 it can be seen that the proportionality between R_p and $I_a^{1/2}$ is maintained for the photopolymerization of EGDMA in SBS block copolymer.

According to this mechanism, autoaccelerative behavior should not occur in the photopolymerization of EGDMA in SBS block copolymer given that k_t and k_p remain constant until high conversions. Effectively, no change which denotes autoaccelerative behavior, as it occurs in bulk photopolymerization of EGDMA (Figure 1a), was observed in the upward part of the curve of Figure 1b.

Figure 4 shows the experimental values of k_t, k_p, and k_t/k_p as a function of double-bond conversion for the photopolymerization of EGDMA in SBS block copolymer, polystyrene (PS), and 1,4-*cis*-polybutadiene (PB). Independently of the type of polymer used as binder, the obtained results are very similar, with the reaction diffusion being the mechanism of the termination reaction from the beginning of the polymerization reaction until relatively high double-bond conversions.

Conclusions

The aim of this work was to investigate the mechanism of the termination reaction in the photopolymerization of methacrylic monomers, di- and tetrafunctional, in a polymeric medium. It was found that reaction diffusion was the only mechanism for the termination reaction from the onset of the polymerization until reaching high double-bond conversions for both monomers and using three different polymers—SBS, PS, and PB—as binders. This behavior was different from those previously reported for bulk difunctional monomer polymerizations and bulk polymerizations of multifunctional monomers. In linear polymerizations of difunctional monomer, the reaction diffusion controlled the termination process only after a 40−50% conversion was reached; in bulk polymerizations of multifunctional monomers, the reaction diffusion started to control the termination reaction early, at approximately 10% double-bond conversion. In the present case of polymerization of di- and tetrafunctional methacrylic monomers in a polymeric medium, the termination process is controlled by reaction diffusion right from the beginning of the polymerization reaction. Also, the relationship between k_t and k_p was studied, and a linear relationship of these kinetic constants was found from the beginning of the polymerization reaction.

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