Photoinitiated Polymerization of Di- and Tetrafunctional Methacrylic Monomers in a SBS Matrix. Kinetic, Mechanistic, and Structural Aspects

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Received October 26, 1998; Revised Manuscript Received May 21, 1999

ABSTRACT: The kinetics and mechanism of the photoinitiated polymerization of tetrafunctional and difunctional methacrylate monomers (di-, hexa-, and decamethylene dimethacrylates; and ethylhexyl and dodecyl methacrylates) in a styrene−butadiene−styrene (SBS) block copolymer matrix have been studied. Reaction diffusion was found to be the only termination mechanism for tetrafunctional monomers when the monomer concentration in the matrix is below 30−40%; for higher monomer concentrations, reaction diffusion controls the termination process only after approximately 10% conversion was reached. The values of both the propagation kinetic constant and the overall double bond conversion for the three tetrafunctional monomers studied showed the following order: deca- > hexa- > dimethylene dimethacrylate. The termination process in the photoinitiated polymerization of difunctional methacrylate monomers is clearly controlled by reaction diffusion right from the beginning of the polymerization reaction only at a very low monomer concentration in the matrix (10−15%); for medium monomer concentrations (20−40%), a combination of both mechanisms, segmental diffusion-controlled (autoaccelerated kinetics) and reaction diffusion, was observed until reaching a double bond conversion of 20%, from which point reaction diffusion predominated; for higher monomer concentrations (60−90%), the termination kinetic constant values at low conversions (<30%) were close to those corresponding with standard polymerizations, observing the Trommsdorff effect (autoacceleration) at higher double bond conversions. The SBS matrix participates appreciably in the polymerization process through the direct addition of the macroradical or the primary radical to the double bond of the polybutadiene moiety and through hydrogen abstraction from the matrix with the formation of benzylic and allylic radicals.

Introduction

Polymer photochemistry has received special attention over the past decade due to the large number of possible applications, and within this area, photoinduced polymerization and photo-cross-linking reactions have reached significant importance with strong applications in such diverse fields as coatings,[1] optical devices,[2] microelectronics,[3] graphics arts,[4] etc. For many of these applications, principally those linked with image formation, a polymeric matrix or 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 in many cases determine the end use of the photopolymer.

There is a large body of information in the literature on thermal and photochemical bulk cross-linking polymerization of polyfunctional monomers,[5−12] but the kinetic, mechanistic and structural problems involved in the study of the photopolymerization−photo-cross-linking reactions in solid polymeric media have not received the same attention.

The pioneering studies of Timpe[13,14] were made by the calorimetric analysis of the photopolymerization of multifunctional acrylic esters in polymeric binders, where some kinetic parameters, such as the maximum rate of polymerization, limiting conversion, inhibition time, and time needed to reach the maximum rate of polymerization, were determined. More recently, Decker et al.[15,16] studied the photoiniated polymerization kinetics of acrylic monomers in several matrices (poly(vinyl chloride), polymethyl methacrylate and polyurethane) by IR spectroscopy.

The photoinitiated polymerization of methacrylic monomers shows different kinetic and mechanistic behavior for the three following cases: bulk polymerization of difunctional monomers (monomethacrylates), bulk polymerization of polyfunctional monomers (tetra or higher functionality), and polymerization of methacrylic monomers in a polymeric medium.

In the bulk polymerization of methyl methacrylate (MMA), the Trommsdorff effect sets in after an unperturbed period of about 15−20% conversion. This enables a separation to be made between unperturbed and autoaccelerated kinetics.[3] It was found that the reaction diffusion termination mechanism—a reaction which occurs when the “frozen” polymer radical propagates through the matrix of unreacted functional groups until it encounters a second active chain radical and terminates—became important only after the onset of gelation, typically from 40 to 60% conversion.[17−19]

In bulk polymerizations of multifunctional monomers, reaction diffusion starts to control the termination reaction early, at approximately 10% double bond conversion.[8,9,20] Until that conversion is reached, autoacceleration takes place; the termination kinetic constant, k_t, decreases from the start to aproximately 10% double bond conversion. Above this conversion, k_t values are maintained in a plateau until high double bond conversions are reached.

When reaction diffusion dominates the termination reaction, the termination kinetic constant is found to be proportional to the product of the propagation kinetic constant and the double-bound concentration[6,8,10] ($k_t = C_{RD}k_p[M]$).

10.1021/ma9816721 CCC: $18.00

We have recently described the mechanism which governs the polymerization kinetics of methacrylic monomers at low concentrations (<15%) in a polymeric medium.[20] Reaction diffusion has been suggested as the only mechanism acting throughout the entire polymerization reaction when these monomer concentrations in the matrix are used. The radicals trapped into the matrix add unreacted functional groups until encountering a second radical for termination.

We have also described[21] the photoreactions of 1-heptene, 3-heptenes, and cumene in the presence of unimolecular and bimolecular polymerization photoinitiators (1,1-dimethoxy-1-phenyl-acetophenone, DMPA, and benzophenone, BP, respectively). These compounds were taken as model compounds of the SBS block copolymer, which is used as the polymeric matrix in the present study. The most important results obtained were the following: (i) The main photoreaction induced by BP in heptene derivatives (models of the *cis*-, *trans- and vinyl*-double bonds of the polybutadiene sequence in the SBS block copolymer) is the direct abstraction of an allylic hydrogen atom and, to a minor extent, of other hydrogen atoms of the heptene aliphatic chain. Photoreaction in the presence of DMPA occurs by direct attack of the radicals formed at the heptene double bond; when this double bond is terminal, oligomerization occurs. (ii) For both photoinitiators in cumene (a model for the benzylic position of the polystyrene moiety), the photoreaction takes places through direct hydrogen abstraction in the benzylic position. These results have been useful to analyze photopolymerization profiles using DSC and ESR as monitoring techniques in methacrylic monomer−SBS matrix−photoiniator systems and to identify the photogenerated radicals.[22,23] Allylic and benzylic radicals were detected, and the methacrylic radical is found to propagate from the beginning of the reaction in a state of restricted mobility, thus confirming that the mechanism of photopolymerization in polymeric binders takes place through reaction diffusion.

The aim of the present article is the study of the kinetics and mechanism of the photoinitiated polymerization of di- and tetrafunctional methacrylate monomers in a SBS matrix at different monomer concentrations. The maximum double bond conversion, the maximum polymerization rate, the intrinsic reactivity (intrinsic polymerization rate), the mechanism of the termination reaction, the relationship between kinetic constants and monomer structure, the participation of the matrix in the polymerization reaction, and the structures of the polymerized systems are principally the questions to be analyzed and investigated.

Experimental Section

Materials. Ethylhexyl methacrylate (EHMA), lauryl methacrylate (LMA), ethylene glycol dimethacrylate (EGDMA), and hexanediol dimethacrylate (HDDMA) monomers from Aldrich (98%) were used without further purification. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) photoinitiator from Ciba Geigy was used as received.

Decanediol dimethacrylate (DDDMA), was prepared by reaction of methacrylic acid and 1,10-decanediol, using *p*-toluensulfonic acid as the catalyst. In a typical experiment, approximately 30 mL (0.353 mol) of methacrylic acid, 0.25 g of *p*-toluensulfonic acid, 21.75 g (0.125 mol) of 1,10-decanediol, and 0.05 g of hydroquinone were disolved in 50 mL of toluene in a Dean−Stark glass apparatus; the reaction mixture was heated to reflux and stirred under nitrogen until 4.5 mL of water was separated (≈4 h); after the solvent was removed by distillation under reduced pressure, the product was purified, first by passing it through a column of silica gel using a hexanes−ether (1:1) mixture as eluent, followed by passing it through a column of basic activated silica gel in order to eliminate acid traces. The product was characterized by elemental microanalysis, ^{1}H NMR, and ^{13}C NMR.

Styrene−butadiene−styrene block copolymer (SBS) 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 the following isomeric distribution, 50% 1,4-cis, 40% 1,4-trans, and 10% 1,2-vinyl, was purified by precipitation with methanol from chloroform solution.

Procedure. The polymerization was studied by differential scanning photocalorimetry (photo-DSC) as previously described.[20,24,25] All exposures were undertaken at 40 °C under a nitrogen atmosphere. The samples were irradiated with UV light from a Hanovia medium-pressure mercury lamp, wich incorporated an interference filter with maximum transmission at 365 nm (International Light NB-365).

In the case of monomer concentrations below 30%, cylindrical specimens of 0.56 cm diameter were cut from films approximately 0.05 cm thick, cast from a 20% chloroform solution of the polymer−monomer−photoinitiator system in Petri dishes. For monomer concentrations between 50 and 80%, 20% polymer−monomer−photoinitiator chloroform solutions were directly poured into the sample pan. After solvent separation, cylindrical samples 0.03−0.06 cm thick and 0.65 cm in diameter were obtained. Finally, for monomer concentrations of 90 and 100%, sample quantities of 20 μL of polymer−monomer−photoinitiator and monomer−photoinitiator solutions, respectively, were prepared using a Hamilton 25 μL syringe. A photoinitiator (DMPA) concentration of 1% was used in all of the photoinitiated polymerizations.

Calculation of Kinetic Constants. 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.[9] The mixtures (polymer−monomer−photoinitiator) were homogeneous and transparent.

To determine the individual kinetic constants of the propagation and termination steps, photoinitiated polymerizations offer the unique advantage of controlling the radical generation by simply exposing or shielding the sample from the light source. Once the shutter for the light source is closed, the radical balance reduces to

$$\mathrm{d}[\mathrm{M}^\bullet]/\mathrm{d}t = -2k_\mathrm{t}[\mathrm{M}^\bullet]^2 \tag{1}$$

Integrating, assuming k_t is approximately constant over a small time interval, which is in fact correct in the particular case of the methacrylic polymerization in a polymeric medium as demostrated from the results obtained in this work, and substituting the radical concentration in terms of the rate of polymerization, monomer concentration, and propagation kinetic constant ($R_\mathrm{p} = k_\mathrm{p}[\mathrm{M}][\mathrm{M}^\bullet]$)causes the equation to become

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

The subscripts 0 and *t* (referring to time) used for time (*t*), monomer concentration ([M]) and polymerization rate (R_p) correspond to the beginning of the dark period and some time later in the dark reaction, respectively. At various time intervals, the shutter was closed and the observed decrease in the rate of polymerization was monitored. 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 value of conversion (heat of reaction released at a given time divided by the theoretical enthalpy: $\Delta H_t/H_\mathrm{theor}n$, n being the number of double bonds present in the monomer). $R_{\mathrm{p}(t)}$ corresponds to the rate of polymerization at time *t*, measured as the height of the

Table 1. Photoinitiated Polymerization of EGDMA in SBS at Different Monomer Concentrations

% M	[M] (M L^{-1})	$I_a \times 10^5$ (einstein L^{-1} s^{-1})	$R_p \times 10^2$ (M L^{-} s^{-1})^a	R_p/[M] $\times 10^2$ (s^{-1})^{a,b}	$k_p/k_t^{1/2}$ (L$^{1/2}$ M$^{-1/2}$ s$^{-1/2}$)^a	% overall double bond convn	ϕ_p
10	0.50	11.85	1.17	2.3	2.57	58	99
20	1.03	11.33	2.94	2.9	3.14		260
50	2.44	4.43	2.20	1.4	1.63	55	500
80	3.91	4.44	3.19	1.3	1.42	56	725
90	4.40	5.04	4.74	1.6	1.77	58	948
100	5.30	6.40	6.20	1.6	1.74	58	967

[a] Measured at the maximum polymerization rate. [b] Corrected values for the same I_a, assuming $R_p \propto I_a^{1/2}$.

Table 2. Photoinitiated Polymerization of HDDMA in SBS at Different Monomer Concentrations

% M	[M] (M L^{-1})	$I_a \times 10^5$ (einstein L^{-1} s^{-1})	$R_p \times 10^2$ (M L^{-} s^{-1})^a	R_p/[M] $\times 10^2$ (s^{-1})^{a,b}	$k_p/k_t^{1/2}$ (L$^{1/2}$ M$^{-1/2}$ s$^{-1/2}$)^a	% overall double bond convn	ϕ_p
10	0.36	10.01	1.62	4.5	5.30	66	161
20	0.78	12.26	3.69	4.2	5.10	69	300
35	1.23	9.72	4.28	3.5	4.22		440
60	2.37	5.85	4.54	2.5	3.00		776
90	3.20	4.60	5.17	2.4	2.85	66	1123
100	3.91	4.99	6.80	2.5	2.94	69	1362

[a] Measured in the maximum polymerization rate. [b] Corrected values for the same I_a, assuming $R_p \propto I_a^{1/2}$.

Table 3. Photoinitiated Polymerization of DDDMA in SBS at Different Monomer Concentrations

% M	[M] (M L^{-1})	$I_a \times 10^5$ (einstein L^{-1} s^{-1})	$R_p \times 10^2$ (M L^{-1} s^{-1})^a	R_p/[M] $\times 10^2$ (s^{-1})^{a,b}	$k_p/k_t^{1/2}$ (L$^{1/2}$ M$^{-1/2}$ s$^{-1/2}$)^a	% overall double bond convn	ϕ_p
10	0.29	10.17	1.40	4.7	5.61	82	137
20	0.64	10.97	2.87	4.3	5.13	82	261
35	1.00	9.69	4.16	4.2	5.02		429
60	1.97	6.94	5.16	3.1	3.74	80	743
90	2.73	5.78	5.53	2.6	3.21	77	956
100	3.11	5.67	7.40	3.2	3.79	77	1305

[a] Measured in the maximum polymerization rate. [b] Corrected values for the same I_a, assuming $R_p \propto I_a^{1/2}$.

exothermic curve at that time. $k_p/k_t^{1/2}$ was calculated from the general kinetic equation

$$R_p = k_p/k_t^{1/2}[M]I_a^{1/2}\phi_i^{1/2} \qquad (3)$$

where I_a is the intensity absorbed 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).[26] A value of 0.7 was found for the initiation quantum yield[20] (ϕ_i) and this value was used in all of the photopolymerizations carried out with the methacrylic monomers studied in this work.

Results

Tetrafunctional Methacrylate Monomers−SBS Matrix Systems. (A) Kinetic and Mechanistic Data. From the polymerization curves obtained by differential scanning photocalorimetry, the kinetic parameters of the photoinitiated polymerization of EGDMA, HDDMA, and DDDMA in the SBS block copolymer at several monomer concentrations (polymerization rate, intrinsic reactivity R_p/[M], $k_p/k_t^{1/2}$ ratio, overall double bond conversion, and polymerization quantum yield) were calculated (Tables 1−3), and from the curves corresponding to the dark reactions (two representative examples are given in Figure 1), the absolute kinetic constants, k_t and k_p, were determined (Figures 2−4).

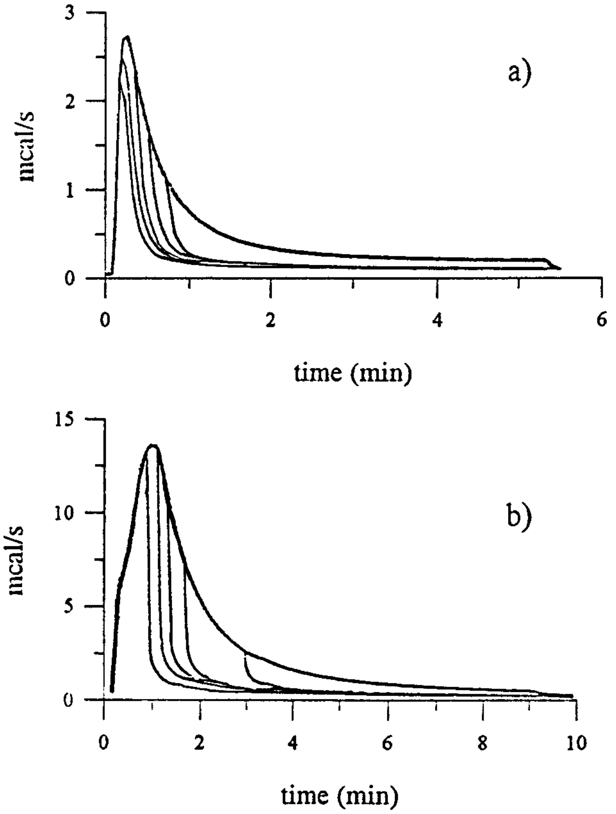

Figure 1. Rate of polymerization as a function of time for different dark reactions during the photoinitiated polymerization of EGDMA in SBS matrix. Monomer concentration in the matrix: (a) 10%; (b) 90%.

(B) Solubility Data. Polymerized EGDMA−SBS and DDDMA−SBS systems with a 20% monomer concentration were immersed in chloroform in order to determine solubilities, gel percentages, sorption data, equilibrium sorptions, etc. Table 4 shows the results obtained. In both systems, soluble fractions were not observed, and therefore the above-mentioned polymerized systems can be considered as cross-linked polymers (100% gel).

Difunctional Methacrylic Monomers−SBS Matrix Systems. (A) Kinetic and Mechanistic Data. Representative polymerization exotherms for several dark reactions are shown in Figure 5 (20, 60, and 90% EHMA concentrations and 20% LMA concentration)

From the polymerization curves obtained by differential scanning photocalorimetry, the same parameters as for tetrafunctional monomers were calculated (Tables 5 and 6, and Figures 6 and 7).

(B) Solubility Data. Table 7 includes data corresponding to the cross-linked fractions of the EHMA−SBS and LMA−SBS systems (20% monomer concentrations) after polymerization.

Analysis and Discussion

Tetrafuncional Methacrylic Monomer−SBS Matrix Systems. (A) Kinetics and Mechanism. As one can observe from Tables 1−3, higher intrinsic reactivities, (R_p/[M]), at the maximum rate of polymerization at monomer concentrations in the matrix below 30−40% are reached (Figure 1), which is due to different mechanisms of termination below and above those monomer concentrations in the matrix, as will be explained later.

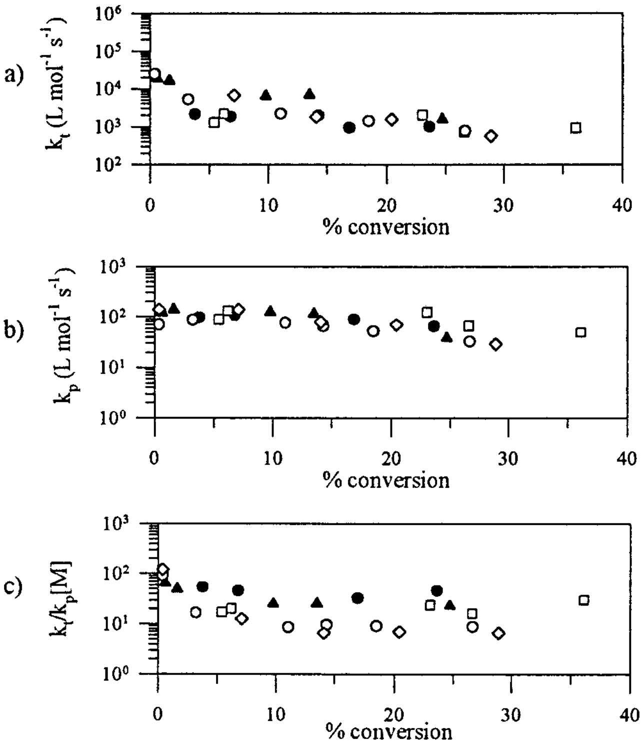

Figure 2. (a) Termination kinetic constant, k_t, (b) propagation kinetic constant, k_p, and (c) ratio of k_t/k_p[M] vs double bond conversion for the photoinitiated polymerization of EGDMA in SBS (see Table 1). Monomer concentration: (●) 10%; (□) 20%; (▲) 50%; (○) 80%; (◇) 90%.

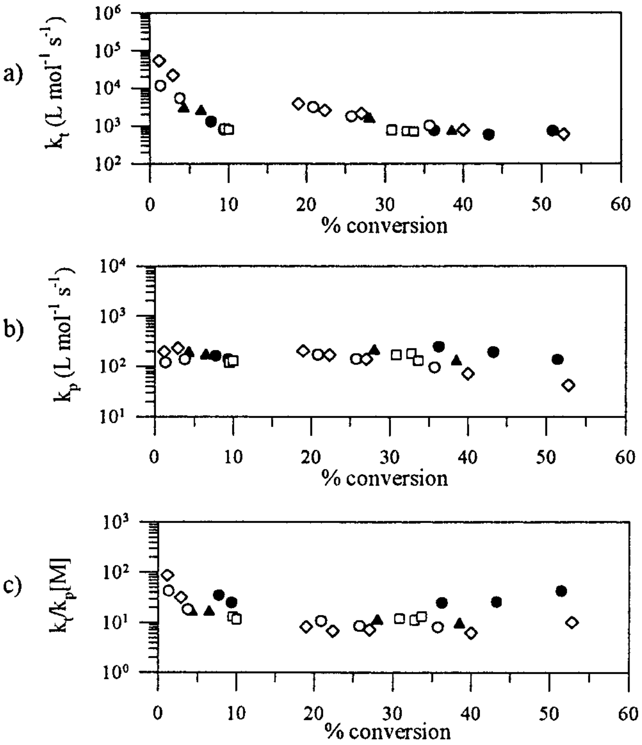

Figure 3. (a) Termination kinetic constant, k_t, (b) propagation kinetic constant, k_p, and (c) ratio of k_t/k_p[M] vs double bond conversion for the photoinitiated polymerization of HDDMA in SBS (see Table 2). Monomer concentration: (●) 10%; (□) 20%; (▲) 50%; (○) 80%; (◇) 90%.

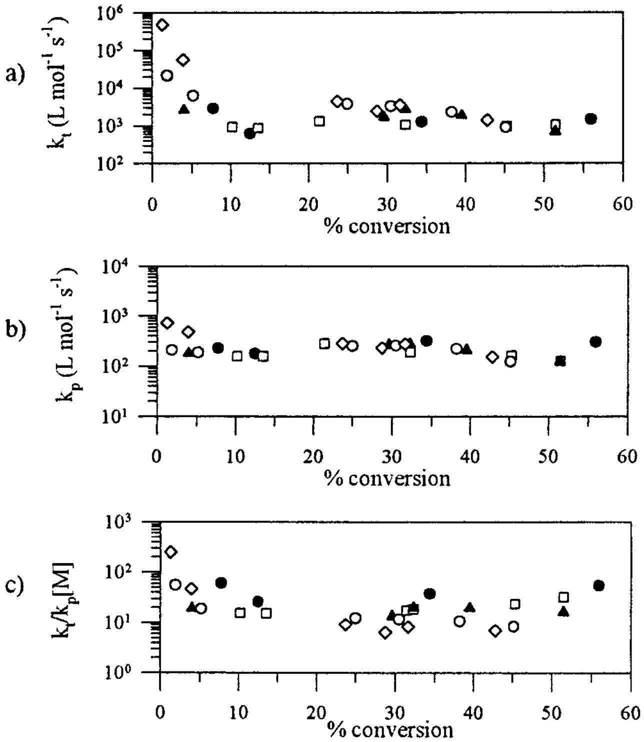

Figure 4. (a) Termination kinetic constant, k_t, (b) propagation kinetic constant, k_p, and (c) ratio of k_t/k_p[M] vs double bond conversion for the photoinitiated polymerization of DDDMA in SBS (see Table 3). Monomer concentration: (●) 10%; (□) 20%; (▲) 35%; (○) 60%; (◇) 90%.

Table 4. Swelling and Cross-Linking (Gel Formation) of the Polymerized SBS−EGDMA and SBS−DDDMA Systems[a]

system	M_0 (g)	M_{eq} (g)	M_{CHCl_3} (g)	M_f (g)	gel %
SBS−EGDMA	0.0169	0.0711	0.0542	0.0163	97
SBS−DDDMA	0.0169	0.0800	0.0631	0.0165	98

[a] Monomer concentration in the SBS matrix: 20% of M_0 (weight of the dry sample before sorption). M_f: weight of the dry sample after desorption. M_{eq}: weight of the swelled sample in the equilibrium. M_{CHCl_3}: weight of absorbed chloroform.

It can also be observed that the intrinsic reactivity increases with the number of methylene groups in the monomer (DDDMA > HDDMA > EGDMA), which is a consequence of the value of the propagation kinetic constant ($k_{p(DDDMA)} > k_{p(HDDMA)} > k_{p(EGDMA)}$) (Figures 2−4). The overall double bond conversion also follows a similar dependence on the number of methylene groups in the monomer, as expected, given that the average molecular weight between junction points of the cross-linked polymer system increases as the number of methylene groups between methacrylate groups increases, which permits a greater monomer mobility until higher conversions are reached.

The assesment of Figures 2−4 leads to some interesting conclusions related to the kinetics and mechanism of the photoinitiated polymerization of tetrafunctional methacrylic monomers in a SBS matrix. In the case of monomer concentrations in the polymeric matrix below 30−40%, the termination process is controlled by reaction diffusion right from the beginning of the polymerization reaction. The k_t values are low (1000−2000 L mol^{-1} s^{-1}) and they remain in a plateau up to high conversions and the k_t/k_p[M] ratio remains almost constant over the whole polymerization reaction. When higher monomer concentrations in the matrix are used, the mechanism of the termination process is controlled by the segmental diffusion of the macroradicals (auto-accelerated kinetics) until a 10% conversion is reached. The k_t value decreases in this interval until reaching a

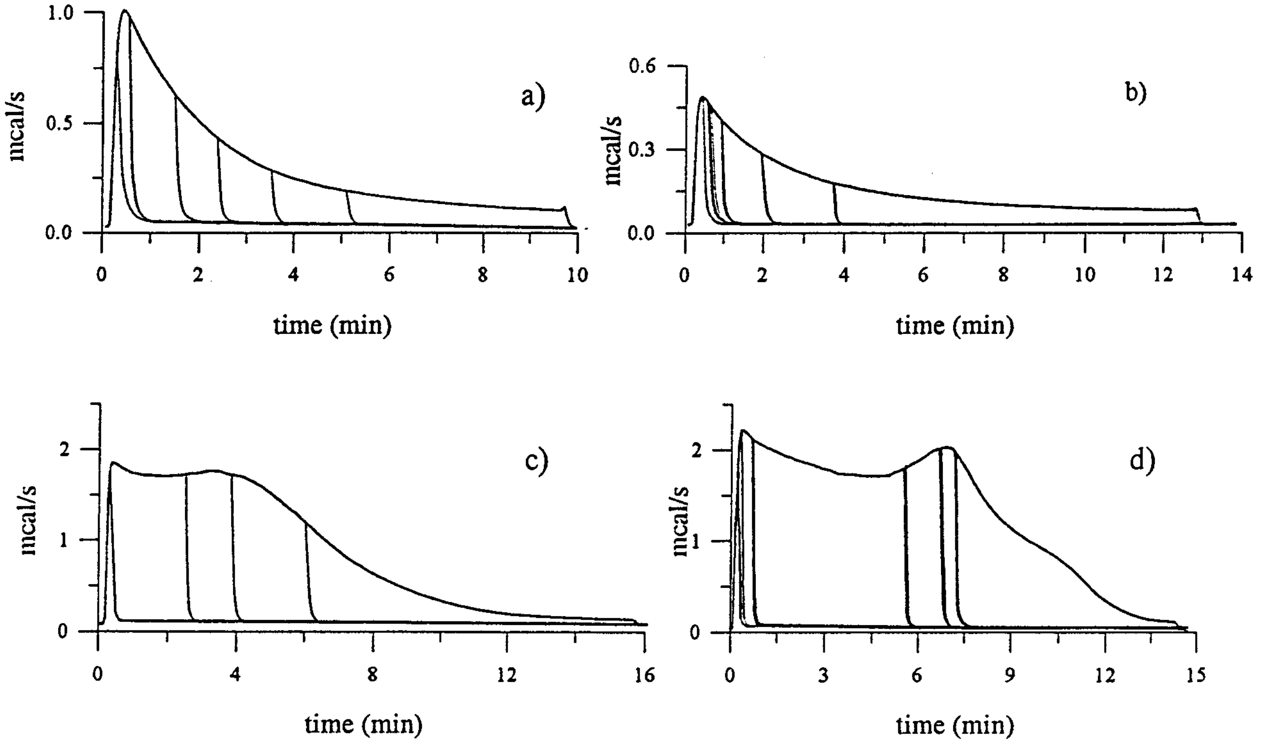

Figure 5. Rate of polymerization as a function of time for different dark reactions during the photoinitiated polymerization of EHMA and LMA in SBS matrix. EHMA concentration in the matrix: (a) 20%; (c) 60%; (d) 90%. LMA concentration in the matrix: (b) 20%.

Table 5. Photoinitiated Polymerization of EHMA in SBS at Different Monomer Concentrations

% M	[M] (M L^{-1})	$I_a \times 10^5$ (einstein L^{-1} s^{-1})	$R_p \times 10^2$ (M L^{-1} s^{-1})^a	R_p/[M] × 10^2 (s^{-1})^{a,b}	$k_p/k_t^{1/2}$ (L$^{1/}$ M$^{-1/2}$ s$^{-1/2}$)^a	% overall double bond convn	ϕ_p
10	0.45	9.97	0.34	0.76	0.78		34
20	0.95	10.27	0.96	1.01	1.20	>95	93
35	1.64	10.84	1.12	0.65	0.78	>95	103
60	2.72	3.46	1.06	0.66	0.79	>95	306
90	4.09	4.09	1.43	0.55	0.59	>95	349
100	4.46	4.43	1.40	0.50	0.56	>95	316

[a] Measured in the maximum polymerization rate. [b] Corrected values for the same I_a, assuming $R_p \propto I_a^{1/2}$.

Table 6. Photoinitiated Polymerization of LMA in SBS at Different Monomer Concentrations

% M	[M] (M L^{-1})	$I_a \times 10^5$ (einstein L^{-1} s^{-1})	$R_p \times 10^2$ (M L^{-1} s^{-1})^a	R_p/[M] × 10^2 (s^{-1})^{a,b}	$k_p/k_t^{1/2}$ (L$^{1/}$ M$^{-1/2}$ s$^{-1/2}$)^a	% overall double bond convn	ϕ_p
10	0.37	10.21	0.32	0.8	1.06		31
20	0.71	9.30	0.54	0.8	0.93	>95	57
35	1.20	9.46	0.82	0.7	0.84	>95	87
60	2.28	6.41	1.04	0.6	0.68	>95	162
90	3.09	5.42	1.41	0.6	0.74	>95	260
100	3.48	4.39	1.60	0.7	0.83	>95	364

[a] Measured in the maximum polymerization rate. [b] Corrected values for the same I_a, assuming $R_p \propto I_a^{1/2}$.

plateau with a value similar to that found for lower monomer concentrations, which means that the termination mechanism from a 10% conversion occurs by reaction diffusion.

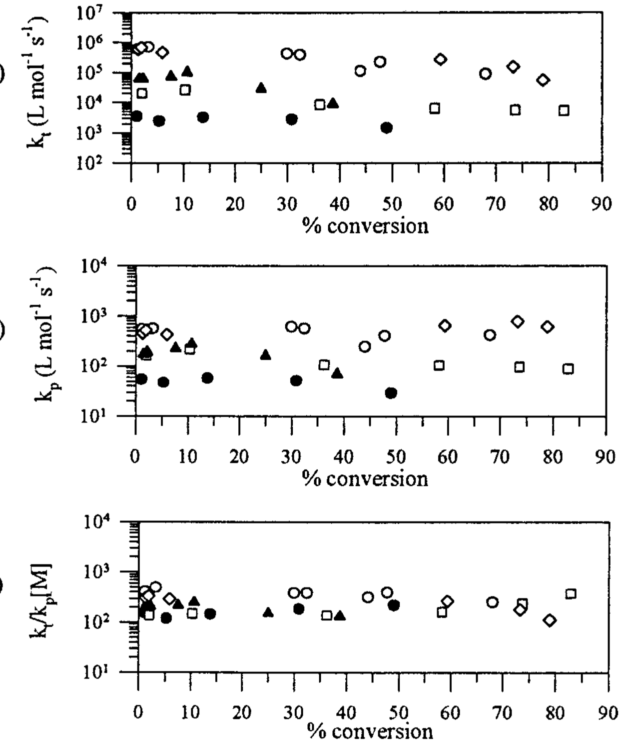

Figure 6. (a) Termination kinetic constant, k_t, (b) propagation kinetic constant, k_p, and (c) ratio of k_t/k_p[M] vs double bond conversion for the photoinitiated polymerization of EHMA in SBS (see Table 5). Monomer concentration: (●) 10%; (□) 20%; (▲) 35%; (○) 60%; (◇) 90%.

According to this mechanism, autoacceleration behavior should not occur in the photopolymerization of tetrafunctional methacrylic monomers in SBS when monomer concentrations are below 30%, given that k_t and k_p remain almost constant until high conversions are reached. Effectively no change, which denotes autoacceleration behavior as for polymerizations carried out at higher monomer concentrations (Figure 1b), was observed in the upward part of the curve of Figure 1a.

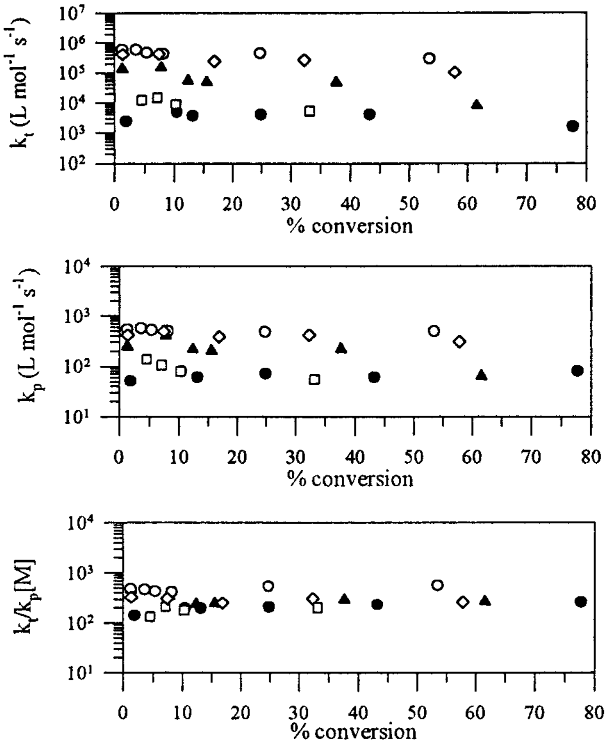

Figure 7. (a) Termination kinetic constant, k_t, (b) propagation kinetic constant, k_p, and (c) ratio of k_t/k_p[M] vs double bond conversion for the photoinitiated polymerization of LMA in SBS (see Table 6). Monomer concentration: (●) 10%; (□) 20%; (▲) 35%; (○) 60%; (◇) 90%.

Table 7. Swelling and Cross-Linking (Gel Formation) of the Polymerized SBS−EHMA and SBS−LMA Systems

system	M_0 (g)	M_{eq} (g)	M_{CHCl_3} (g)	M_f (g)	gel %
SBS−EHMA	0.0147	0.4200	0.4053	0.0097	66
SBS−LMA	0.0142	0.4578	0.4436	0.0092	65

[a] Monomer concentration in the SBS matrix: 20% of M_0 (weight of the dry sample before sorption). M_f: weight of the dry sample after desorption. M_{eq}: weight of the swelled sample in the equilibrium. M_{CHCl_3}: weight of absorbed chloroform.

Another consequence of the observed mechanism is that the intrinsic polymerization rate values, (R_p/[M]), are higher for polymerizations carried out with monomer concentrations below 30−40% (very low k_t values) than for those carried out with higher monomer concentrations (Tables 1−3) as was previously discussed.

(B) Solubility Data. All the systems studied, even those with low monomer concentrations (10 and 20%), yielded cross-linked structures when they were polymerized, which indicates that the SBS matrix participates appreciably in the polymerization process. This participation takes place, according to previous studies,[21−23] and results were obtained here, through hydrogen abstraction in the allylic and benzylic positions of the SBS matrix and by the direct addition of the growing macroradical and the primary radical from the photoinitiator to the double bond of the polybutadiene moiety.

The participation of the binder in the polymerization process prevents phase separation. The polymerized systems were homogeneous and transparent and phase separations were not observed in the polymerized samples analyzed by optical microscopy with polarized light.

Difunctional Methacrylate Monomers−SBS Matrix Systems. (A) Kinetics and Mechanism. From Tables 5 and 6, it can be seen that the double bond conversions in the photopolymerization of EHMA and LMA in SBS matrix reached values close to 100%, as might have been expected for difunctional monomers, which produce less chain mobility restrictions than those found in the tetrafunctional monomers.

As has been described for tetrafunctional monomers, the intrinsic reactivity, R_p/[M], is also greater at low monomer concentrations in the matrix, which must be also associated with a larger contribution of reaction diffusion in the termination reaction at low monomer concentrations, that is a greater value for the $k_p/k_t^{1/2}$ ratio.

With methacrylic difunctional monomers, the termination process was clearly controlled by reaction diffusion right from the beginning of the polymerization reaction up to only a 10% monomer concentration. At 20% monomer concentration a combination of both mechanisms, macroradical segmental diffusion-controlled (autoaccelerated kinetics) and reaction diffusion mechanisms, was observed until reaching a 20% double bond conversion. From this point reaction diffusion predominated (Figures 6 and 7).

For 60% and 90% EHMA concentrations, an important increase of the polymerization rate (parts b and c of Figure 5) was observed at relatively high conversions, due to the gel or Trommsdorff effect. For these concentrations, the termination kinetic constant values at low conversions are close to those corresponding to standard bulk polymerizations of difunctional methacrylic monomers.

(B) Solubility Data. The polymerization of difunctional monomers in a linear polymeric matrix must produce a soluble system if the polymeric matrix does not take part chemically in the polymerization process. That is not the case for the EHMA and LMA polymerizations in a SBS matrix, where, as can be observed in Table 7, a 70% gel fraction was obtained.

When LA was used instead of LMA, a 100% gel fraction was obtained, which was due to the greater reactivity of the polyacrylate radical with respect to the polymethacrylate radical in reacting with the polybutadiene segment of the SBS copolymer through the direct addition of the macroradical to the double bond of the polibutadiene moiety. These results are in agreement with of Sundberg[12] on studies of grafting in free radical copolymerization.

Conclusions

Tetrafunctional Methacrylate Monomer−SBS Systems. Reaction diffusion was the only mechanism for the termination reaction from the onset of the polymerization until reaching high double bond conversions at monomer concentrations in the matrix below 30−40%. At matrix monomer concentrations above 30−40%, reaction diffusion controlled the termination process only after approximately 10% conversion was reached; the termination process mechanism below 10% conversion is controlled by the segmental diffusion of the macroradicals (autoaccelerated kinetics). Figure 8 shows a graphic scheme which indicates the intervals of monomer concentration and double bond conversion where each mechanism takes place.

As a consequence of the data shown, the maximum intrisic polymerization rate, R_p/[M], is conditioned by the termination mechanism. Therefore, higher intrinsic polymerization rates are found at monomer concentra-

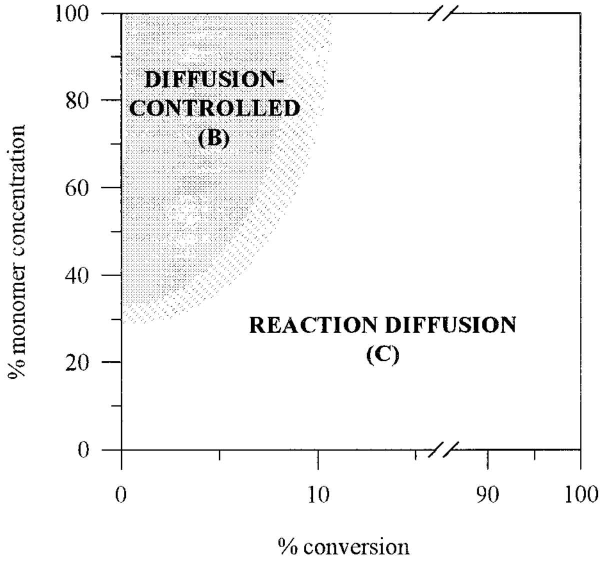

Figure 8. Termination mechanisms in the photoinitiated polymerization of tetrafunctional methacrylic monomers in SBS matrix as a function of the monomer concentration and double bond conversion.

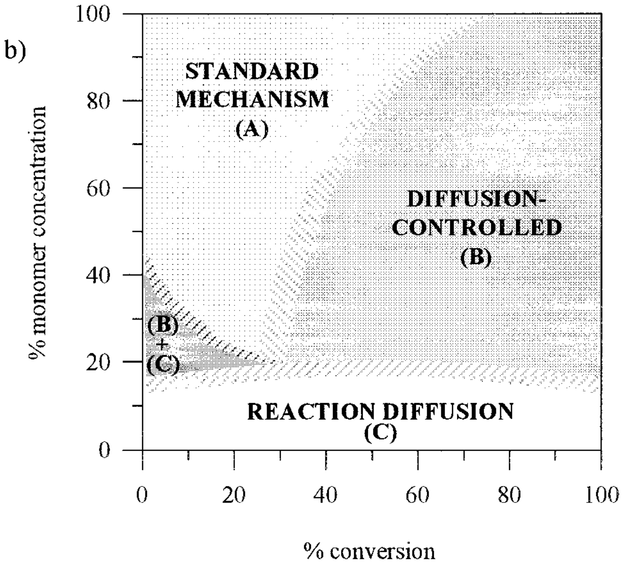

Figure 9. Termination mechanisms in the photoinitiated polymerization of difunctional methacrylic monomers in SBS matrix as a function of the monomer concentration and double bond conversion.

tions below 30–40%, a zone where termination by reaction diffusion takes place.

The values for both the propagation kinetic constant and the overall double bond conversion, for the three tetrafunctional monomers studied, show the following order: DDDMA > HDDMA > EGDMA.

When polymerized, the systems studied, even those with low monomer concentrations, yielded cross-linked structures which indicates that the SBS matrix participates appreciably in the polymerization process. This participation takes place through the abstraction of an allylic hydrogen atom from the polybutadiene segment, by both the growing macroradical and the primary radical from the photoinitiator, through the abstraction of a benzylic hydrogen atom from the polystyrene moiety, and through the direct addition of the macroradical or the primary radical to the double bond of the polybutadiene moiety.

Difunctional Methacrylate Monomer–SBS Systems. The termination process in the photoinitiated polymerization of difunctional methacrylic monomers is clearly controlled by reaction diffusion right from the beginning of the polymerization reaction only at very low monomer concentrations (<10–15%). At 20% monomer concentration in SBS matrix, a combination of both mechanisms, segmental diffusion-controlled (autoaccelerated) kinetics and reaction diffusion, was observed until reaching 20% double bond conversion from which point reaction diffusion predominated. For higher monomer concentrations in the SBS matrix, the termination kinetic constant values at low conversions (<30%) were close to those corresponding to standard polymerizations in solution, observing the Trommsdorff (autoacceleration) effect at higher double bond conversions. Figure 9 shows a graphic as a scheme which indicates the intervals of monomer concentration and double bond conversion at which each mechanism takes place.

The photoinitiated polymerization of EHMA and LMA in SBS matrix at monomer concentrations below 30% yielded transparent, flexible and tough final products. The EHMA–SBS and LMA–SBS systems with only a 20% monomer concentration gave final products with a gel fraction close to 70%, which confirms the participation of the SBS matrix in the polymerization process of methacrylic monomers.

Acknowledgment. Thanks are due to the CICYT (Comisión Interministerial de Ciencia y Tecnología) for financial support (MAT 97-0727).

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MA9816721