Distribution of Mono- and Di-Methacrylic Monomers in SBS Block Copolymer and Its Influence on the Photopolymerization Process

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ABSTRACT: Persoz hardness measurements and the analysis of the temperature dependence of the storage modulus (E′) for SBS di- and tetrafunctional methacrylic monomer systems were carried out to determine the distribution of the monomers in the domains or phases of the SBS block copolymer, as well as the aggregation state of each system. The forces of attraction between the monomer and the phases or domains in the matrix (similar solubility parameters with appreciable dipole-dipole and hydrogen bonding interactions) were determinant as for the monomer distribution.

The influence of these structural factors on the kinetic parameters of the photoinitiated polymerization of di- and tetrafunctional methacrylic monomers in the SBS matrix was studied. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 163–168, 2005

Key words: photoinitiated polymerization; polymeric matrix; dynamic-mechanical properties; Persoz hardness; aggregation state

INTRODUCTION

Photoinduced polymerization and photocrosslinking reactions are important for applications in such diverse fields as coatings,[1] optical devices,[2] microelectronics,[3] and graphic arts.[4] 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 non tacky film or sheet and because the properties of the binder in many cases determine the end use of the photopolymer. One of the more used polymers as a matrix is the styrene-butadiene-styrene block copolymer (SBS), and the obtaining of quantitative data on the distribution of the monomer or monomers in the blocks of the copolymer is of vital importance as for its influence on the polymerization process and, consequently, on the properties of the final product. Complications in the analysis of these systems are due to their micro-heterogeneity, which is retained before and after polymerization, even when relatively high amounts of monomers are introduced. So, for all the studied samples where SBS is used as the matrix, the regular structure corresponding to the matrix is retained after polymerization, that is, the tan δ-temperature spectra maintain the two peaks corresponding to the glass transition of the polybutadiene blocks and, at

higher temperature, that corresponding to the glass transition of the stiff polystyrene blocks.[5]

We have recently published several articles[6−9] about the photoinitiated polymerization of methacrylic monomers in polymeric matrices (SBS, PS, PB, and PMMA). In general, and according to the aforementioned previous articles, it can be said that the mechanism and kinetics of polymerization of methacrylic monomers in polymeric matrices differ from those in bulk and solution polymerization and depend on several factors: 1) aggregation states (rubbery or vitreous) of the monomer-matrix systems; 2) compatibility between the monomer and the matrix, and between the formed polymer and the matrix; 3) forces of attraction between the monomer and the matrix, and between the growing macroradical and the matrix; and 4) participation of the matrix in the polymerization process. For systems where a relatively high intermolecular force of attraction between the monomer and the matrix occurs (similar solubility parameters with appreciable dipole-dipole and hydrogen bonding interactions[9]), a reaction diffusion termination mechanism takes place right from the beginning of the polymerization process until high monomer conversions. Examples of systems with this behavior are: polystyrene-hexanedioldimethacrylate (PS-HDDMA)[6] and polymethylmethacrylate-hexanedioldimethacrylate (PMMA-HDDMA).[9] Reaction diffusion occurs when the "frozen" polymer radical propagates through the matrix by reaction with unreacted functional neighboring groups until it encounters a second active chain radi-

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cal and terminates. The termination kinetic constant value found for the polymerizations in which the reaction-diffusion mechanism clearly predominates[6–11] was several orders of magnitude lower than that corresponding to a standard polymerization (10^3 vs. 10^6 L mol^{-1}s^{-1}); consequently, the intrinsic reactivity (R_p/[M]) and $k_p/k_t^{1/2}$ values are higher than those for the standard polymerizations.

The photoinitiated polymerization of methacrylic monomers in polymeric matrices usually permits an improved homogeneity of polymer blends obtained through a reduction of the domain sizes of the phases. When polybutadiene (PB) and SBS are used as matrices, crosslinked polymerized products are obtained as a consequence of the participation of double bonds of the matrix in the polymerization process (copolymerization). Polystyrene (PS) sequences in the SBS matrix[6,7] also take part in the polymerization process through the coupling of the benzylic radical to the growing macroradical.

In this study, studies are carried out to determine the distribution of the di- and tetrafunctional methacrylic monomers in the domains or phases of the SBS matrix and the state of aggregation for each system, as well as the influence of these structural factors on the polymerization process. The values of hardness and dynamic mechanical measurements have been used to analyze and investigate these questions.

EXPERIMENTAL

Materials

2-Ethylhexyl methacrylate (EHMA), 1,6-hexanediol dimethacrylate (HDDMA), and ethylene glycol dimethacrylate (EGDMA) monomers from Aldrich (98%) were used without further purification.

Styrene-butadiene-styrene block copolymer (SBS) denoted as C-501 (Repsol YPF) 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.

Sample preparation, measurements, and kinetic parameters

The samples for hardness and dynamic mechanical measurements were cut from films 0.08–0.10 cm thick, cast from a 20% chloroform solution of the SBS-methacrylate monomer system in Petri dishes. The notation used below for the samples includes the matrix and the monomer used and the concentration of the monomer in %w/w between parentheses, for example: SBS-HDDMA (20).
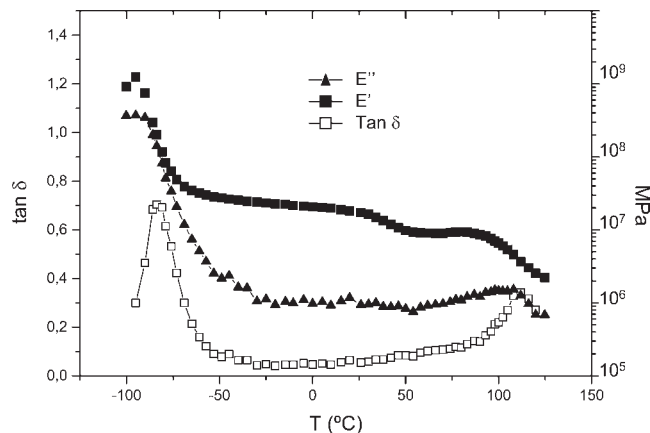

Figure 1 Temperature dependence of the dynamic mechanical measurements for the SBS block copolymer.

The hardness was evaluated according to the Pendulum Hardness, Persoz method (Neurtek S.A.). Dynamic mechanical measurements were made with a Metravib RAC 815A viscoanalyzer under an oscillatory tensile deformation with a dynamic amplitude of 2 μm. Samples of approximately 1×2 cm and 0.08–0.09 cm thick were scanned at 5Hz.

The kinetic parameters used in this paper were taken from the aforementioned articles.[6–9]

RESULTS AND DISCUSSION

Hardness and dynamic mechanical measurements

The temperature dependence of the dynamic mechanical measurements (storage modulus, E′, loss modulus, E″, and tan δ) corresponding to SBS block copolymers used in this work is shown in Figure 1. The spectra are in accordance with the two microphases that this block copolymer shows. In agreement to the solubility parameters values of the methacrylic monomers and the homopolymers (PS and PB) that form the SBS block copolymer,[9] it sets as assumption that the tetrafunctional monomers will show a higher affinity for the PS blocks (solubility parameters, δ, for EGDMA, HDDMA, and PS are 18.7 MPa$^{1/2}$, 17.9 MPa$^{1/2}$, and 18.7 MPa$^{1/2}$, respectively), and the difunctional monomer for those of PB (solubility parameters, δ, for EHMA and PB are 16.8 MPa$^{1/2}$ and 17.1 MPa$^{1/2}$, respectively). To confirm these assumptions and correlate them with the kinetic parameters obtained in the photoinitiated polymerization of these systems, the following studies were carried out.

Dynamic mechanical measurements

The temperature dependence of the storage modulus (E′) for the SBS-EGDMA, SBS-HDDMA, and SBS-
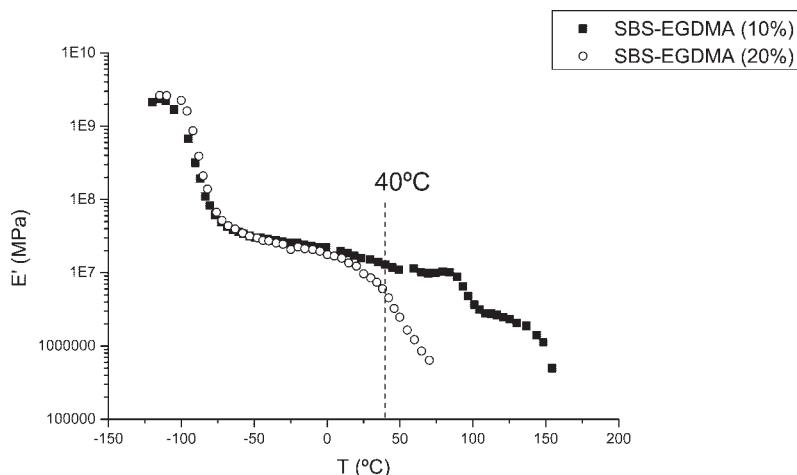
Figure 2 Temperature dependence of the storage modulus (E′) for the SBS-EGDMA (10) and SBS-EGDMA (20) systems.

EHMA systems at 10 and 20% monomer concentrations are shown in Figures 2, 3 and 4.

For the SBS-EGDMA system, a sharp decrease of the modulus value is appreciated at lower temperatures than for the unmodified SBS matrix, and it depends on the concentration of monomer in the system. The change in the slope occurs at temperatures around 20–30°C for an EGDMA concentration of 20% and of 80–90°C for the system with 10% concentration; these temperature values at which a decreasing of the storage modulus is observed correspond with the vitreous transitions temperatures of the PS blocks plasticized with EGDMA monomer. Taking into account that the polymerization studies have been carried out at 40°C, the SBS-EGDMA (10) system will react maintaining the PS segments plasticized with the monomer in the vitreous state ($T_g > 40$°C), while for the system that contains 20% monomer concentration, the PS blocks will be in the rubbery state ($T_g < 40$°C). This will have,

without a doubt, an important influence on the polymerization kinetics, as will be seen below.

For the SBS-HDDMA systems (Fig. 3), the drop of the storage modulus (E′) occurs at lower temperature than that corresponding to the SBS-EGDMA system, which is due to the greater plasticizing capacity for the HDDMA monomer compared to the EGDMA monomer. The higher the intermolecular attraction force between the plasticizer (monomer) and the polymer, mainly due to dipole-dipole and hydrogen-bonding interactions, the lower additional free volume is generated and, consequently, the decreasing of the vitreous transition temperature will be smaller. As a consequence, the vitreous transition temperature of the polystyrene domains in this system drops below the polymerization temperature, 40°C, for all the used monomer concentrations, and therefore, the polymerization reaction in the SBS-HDDMA system will take place with the PS phase in the rubbery state.
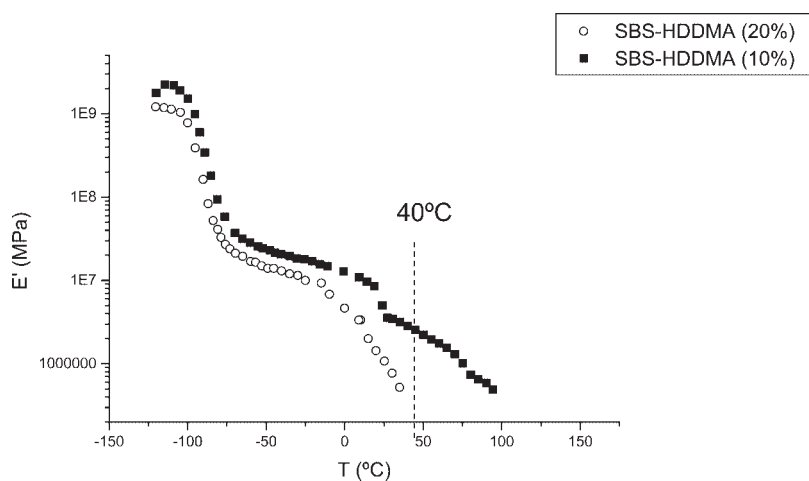

Figure 3 Temperature dependence of the storage modulus (E′) for the SBS-HDDMA (10) and SBS-HDDMA (20) systems.
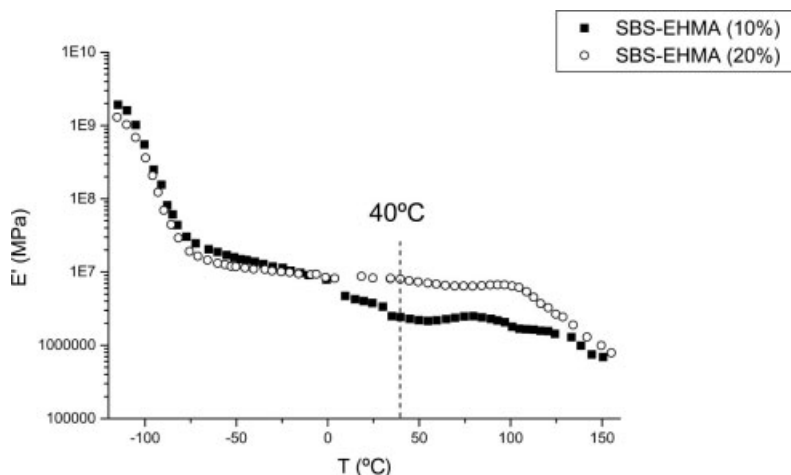
Figure 4 Temperature dependence of the storage modulus (E′) for the SBS-EHMA (10) and SBS-EHMA (20) systems.

Experimentally, SBS-tetrafunctional methacrylic monomer system samples showed poor dimensional consistency; plots of tan δ and loss modulus values versus temperature were very scattered and non reproducible, and for this reason they were not included. In addition, the intent of measuring the vitreous transition temperatures for the SBS-tetrafunctional methacrylic monomer systems through DSC analysis did not result, because changes in the slope of the calorimetric curve in the area corresponding to the polystyrene blocks were not observed. However, the vitreous transition temperatures for the PS-HDDMA and PS-EHMA systems can be correctly measured by DSC.[7] T_g values for the systems with PS matrix, for a monomer concentration of 10%, were between 45 and 50°C for both monomers. T_g value for the PS-HDDMA (20) system was around 25–30°C and 10°C for the PS-EHMA (20) system. This means that both systems are in the rubbery state to the polymerization temperature for a monomer concentration of 20% and in the vitreous state when the monomer concentration is of 10%. These results agree with the assumption of the predominant accumulation of the tetrafunctional methacrylic monomers in the PS domains of SBS block copolymers. Effectively, the rubbery state for the SBS-HDDMA (10) system and the vitreous state for the PS-HDDMA (10) system to the polymerization temperature (40°C) means that the monomer concentration in the PS domains of the SBS matrix is appreciably higher than that corresponding to the PS-HDDMA system.

For the system SBS-EHMA, it must be expected that there will be a higher accumulation of monomer in the PB domains of the SBS matrix considering that the solubility parameters of the monomer (EHMA) and PB are very similar, 16.8 and 17.1 $MPa^{1/2}$, respectively, and that, on the other hand, there is an important difference between the monomer and PS solubility parameter values, 16.8 and 18.7 $MPa^{1/2}$. Effectively, there is no decreasing of the storage modulus (Fig. 4) observed below 90°C, which means that the PS domains remain without appreciable change as a consequence of the practically total incorporation of the monomer (EHMA) in the PB domains.

Persoz hardness measurements

The hardness of the SBS-methacrylic monomer systems was evaluated by monitoring the damping of the oscillations of a pendulum (Persoz hardness). The physical significance of pendulum hardness has been reviewed by Sato.[12] The theory predicts that pendulum hardness is not a general measure of hardness, but substantially, a value proportional to the reciprocal of the damping capacity or mechanical loss. Therefore, it is meaningless to compare the rigidities of coating films composed from materials of different viscoelastic properties by pendulum hardness, and the

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TABLE I
Persoz Hardness for the SBS-EGDMA System

Monomer %	Persoz hardness
0	148
10	128
20	22

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TABLE II
Persoz Hardness for the SBS-HDDMA System

Monomer %	Persoz hardness
0	146
10	58
20	28

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TABLE III
Persoz Hardness for the SBS-EHMA System

Monomer %	Persoz Hardness
0	148
10	137
20	118

validity of pendulum hardness is restricted to homologous materials. However, the pendulum method may be reasonably used for measuring the viscoelastic properties of films or sheets.

The Persoz hardness values obtained for the SBS-EGDMA, SBS-HDDMA, and SBS-HEMA systems (Tables I, II, and III) confirm the conclusions obtained by dynamic mechanical measurements in relation to the distribution of the monomers in the PS and PB domains of the SBS matrix. A sharp decreasing of the Persoz hardness value for the SBS-EGDMA system is observed (Table I) when passing from a monomer concentration of 10% to another of 20%, which seems to reflect a change in the aggregation state, from vitreous to rubbery, when passing from a concentration to another, such as was observed through the dynamic

mechanical measurements. For the SBS-HDDMA system, the drastic drop of the Persoz hardness (Table II) is already observed for a monomer concentration of 10%. Finally, for the SBS-EHMA system, there are no sharp changes in the Persoz hardness values (Table III), which supports the idea that this monomer (EHMA) is accumulated principally in the PB domains.

Monomer distribution and photopolymerization kinetic parameters

Kinetic parameters for the photoinitiated polymerization of the different monomer-matrix systems are shown in Table IV.

The analysis of the data permits correlation of the polymerization process kinetic parameters with the above investigated structural characteristics of the SBS-methacrylic monomer systems (distribution of the monomer and aggregation state).

Effectively, the kinetic and mechanistic behavior of the DBD-EGDMA, SBS-HDDMA, and PS-HDDMA systems in the polymerization process is practically the same, as a consequence of the accumulation of the monomer fundamentally in the PS domains of the SBS

TABLE IV
Comparative Kinetics Data of the Photoinitiated Polymerization of Methacrylic Monomers in SBS, PS, and PB Matrices

Polymerization system	$[M]$ $L \cdot mol^{-1}$	$R_p/[M] \times 10^2(s^{-1})$	$k_t \times 10^{-3}$ $(Lmol \cdot s^{-1})$	k_p $(Lmol \cdot s^{-1})$	Comments
SBS-EGDMA	10	2.0	1.4	96	Vitreous state for PS domains. Reaction diffusion termination.
	20	2.9	1.6	130	Rubbery state for PS domains. Reaction diffusion termination.
	50	1.4	17	212	Rubbery state for PS domains. Reaction diffusion termination.
	>50	1.3–1.6	30–100	600	Rubbery state for PS domains. Reaction diffusion termination.
SBS-HDDMA	10	4.5	1.0	150	Rubbery state for PS domains. Reaction diffusion termination.
	20	4.3	0.8	120	Rubbery state for PS domains. Reaction diffusion termination.
	35	3.5	2.5	175	Rubbery state for PS domains. Reaction diff + diffusion controlled.
	>35	2.1	>10	175	Rubbery state for PS domains. Reaction diff + diffusion controlled.
PS-HDDMA	10	1.9	1.0	45	Vitreous state. Reaction diffusion termination.
	20	4.4	1.4	170	Rubbery state. Reaction diffusion termination.
	35	4.7	2.5	250	Rubbery state. Reaction diff + diffusion controlled.
	>35	2.5	>10	250	Rubbery state. Reaction diff + diffusion controlled.
SBS-EHMA	20	1.0	25	200	Vitreous state for PS domains. EHMA in PB domains.
	35	0.6	75	210	Vitreous state for PS domains. EHMA in PB domains.
	>35	0.5–0.7	>500	500	Viscous state. Practic. standard termination.
PB-EHMA	20	0.6	200	500	The polymerization behavior is similar to that of the SBS-EHMA system.
	35	0.6	300	650	
	>35	0.35	>800	600	

matrix: 1) the affinity between monomer and polymer (PS phase or PS homopolymer) determines that reaction diffusion was the only mechanism for the termination reaction from the onset of polymerization until reaching high double bond conversions for low monomer concentrations; and 2) the kinetic parameters, $R_p/$[M] and k_p, varied as a function of the aggregation state of the PS domains, where the monomer is fundamentally accumulated. An appreciable drop of the above-mentioned kinetic parameters values is observed when passing from a system that is in the rubbery state to another in the vitreous state; this behavior is observed for the SBS-EGDMA and PS-HDDMA systems when passing from 20 to 10% monomer concentration.

The kinetic and mechanistic behavior of SBS-EHMA and PB-EHMA systems in the polymerization process are similar, as a consequence of the fact that the monomer is accumulated principally in the PB domains of the SBS matrix. A clear reaction diffusion termination is not observed for low monomer concentration, and a combination of reaction-diffusion and diffusion-controlled mechanisms better explained the behavior of polymerization of these systems for monomer concentration below 30–40%. In these systems, the k_p values are considerably increased because of the greater mobility of the monomer in the matrix (low δ values) and the k_t values approached a standard value ($\approx 10^6$ L mol^{-1} s^{-1}) for monomer concentrations higher than 35%. Given that the polymerization takes place, fundamentally, in the PB domains of the SBS matrix, the vitreous aggregation state of the PS domains in the mentioned matrix does not have a determinant influence on the mechanism of the polymerization process. However, the higher k_p and k_t values that are obtained for system PB-EHMA in comparison to the SBS-EHMA system seem to reflect a higher difficulty of translation for the macroradical and the monomer in the SBS-EHMA system.

On the other hand, there is an important difference among intrinsic reactivities ($R_p/$[M]) of the SBS-HDDMA and PS-HDDMA systems and those of the SBS-EHMA and PB-EHMA systems, principally for low monomer concentrations. This is a consequence of the different termination mechanism of the polymerization: reaction diffusion termination versus a combination of reaction-diffusion termination and diffusion-controlled termination.

CONCLUSIONS

The distribution of the monomers in the domains or phases of the SBS block copolymer depends fundamentally on the forces of attraction between the monomer and the phase o domain. The similarity of the solubility parameters of both monomer and phase was decisive in relation to that distribution. So, the tetrafunctional methacrylic monomers accumulate preferably in the PS domains, while the difunctional monomer with long hydrocarbonated chain accumulates preferably in the PB domains.

The aggregation state of the PS phase in the SBS block copolymer equally depends on the affinity between the monomer and the PS phase and, consequently, of the similarity among solubility parameters. These structural factors, monomer distribution and aggregation state, determine the mechanism and kinetics of polymerization. This way: 1) reaction diffusion was the only mechanism for the termination reaction from the onset of polymerization for low monomer concentrations for the SBS-EGDMA, SBS-HDDMA, and PS-HDDMA systems as a consequence of the strong attraction between the tetrafunctional monomer and the PS phase; 2) the kinetic behavior of polymerization of the SBS-EGDMA, SBS-HDDMA, and PS-HDDMA systems is very similar as a consequence of the accumulation of monomer in the PS phase of the SBS matrix—and something similar occurs for the SBS-EHMA and PB-EHMA systems where the accumulation takes place in the PB domains; and 3) an appreciated drop of the $R_p/$[M] and k_p values is observed when passing from a system with PS domains in the rubbery state to another in the vitreous state, behavior observed for the SBS-EGDMA and PS-HDDMA systems when passing from 20 to 10% monomer concentration.

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