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Polymer 43 (2002) 3173–3179

polymer

www.elsevier.com/locate/polymer

Preparation of poly(*tert*-butyl acrylate-*g*-styrene) as precursors of amphiphilic graft copolymers. 1. Kinetic study and thermal properties

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Received 3 September 2001; received in revised form 19 December 2001; accepted 11 February 2002

Abstract

Free radical copolymerizations of *tert*-butyl acrylate and a polystyrene macromonomer carrying a methacryloyloxy group at the chain end have been performed in benzene solution using 2,2′-azobis(isobutyronitrile) (AIBN) as initiator at 70 °C. The estimated values of the 'lumped' kinetic constant, $k_p/k_t^{1/2}$, have shown a clear dependency on the macromonomer concentration in the reaction medium. The obtained poly(*tert*-butyl acrylate-*g*-polystyrene) graft copolymers were characterized by size exclusion chromatography (SEC), and differential scanning calorimetry (DSC). In addition, the thermal behavior of these copolymers was studied by thermogravimetric analysis (TGA). Subsequently, hydrolysis of precursor graft copolymer was performed to afford an amphiphilic graft copolymer. Characterization using FT-IR confirmed total hydrolysis of the ester group. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*tert*-butyl acrylate-*g*-polystyrene) graft copolymers; Kinetic; Size exclusion chromatography

1. Introduction

Grafting has been utilized as an important technique to modify the chemical and physical properties of polymers [1]. Graft copolymers have been extensively studied from both useful properties and applications. They can be used for a wide variety of applications, such as surfactants, compatibilization agents in polymer blends, additives in high impact materials, enhanced tensile strength, adhesives, improved metal adhesion, controlled wettability, better pigment dispersion, enhanced thermal stability, thermoplastic elastomers, etc. [2,3] depending on the nature of their backbone and side chains, besides the molecular weight (MW) or/and molecular weight distribution (MWD) and other grafting parameters.

Ionic polymerization techniques permit a better control of the graft copolymer structure although they require stringent conditions, such as, complete absence of moisture and other acidic impurities. As a consequence, most graft copolymers are prepared by free radical polymerization. There are three graft copolymerization methods, 'grafting from', 'grafting onto' and 'grafting through'. The macromonomer technique is one of the 'grafting through' processes most worldwide used. One of the advantages of the macromonomer method is that chain length of the graft is determined by that of the macromonomer, so it can be controlled easily. However, the frequency of branches is determined by the molar ratio of the comonomers and their reactivity ratios [4,5], and the chain length of the backbone is conditioned by typical polymerization parameters, such as monomers and initiator concentrations, temperature, etc.

In addition, it is well known that a great number of these copolymerization processes are conducted in solution because of the mitigation of viscosity-related problems that are manifested in the areas of heat transfer, mixing, and material handling and processing. These features are especially relevant in the case of acrylic acid derivatives polymerizations. Bamford et al. [6] pointed out that the polymerization of these monomers is accompanied by difficulties in the rate measurements. They become very viscous when the polymerization is performed in bulk even at low conversions, due to an autoacceleration process. Therefore, these polymerization reactions are performed in a dilute environment to eliminate or to reduce the Trommsdorff or gel effect. Moreover, some data reveal that the rate coefficient values for homopolymerizations are dependent on the monomer concentration [7–10]. Besides, different rate coefficient values have been obtained for these monomers, even in cases where the reaction conditions are practically identical [11]. Furthermore and to our knowledge, there are no reliable data concerning the homopolymerization of *tert*-butyl acrylate (*t*BA).

On the other hand, it is well known graft as well as block

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PII: S0032-3861(02)00140-4

copolymers present microphase separation depending on their molecular weight and composition, which determine the polymer properties [12]. Some of these copolymers can include hydrophobic and hydrophilic nature and, therefore, present relevant properties in solution. They can form colloidal size aggregates or micelles in a selective solvent and the type of aggregate developed will depend on the balance between hydrophobic and hydrophilic parts [13].

In this sense, this article describes the preparation and characterization of poly(*tert*-butyl acrylate-*graft*-polystyrene) as possible precursors of amphiphilic graft copolymers. The lumped kinetic parameter $k_p/k_t^{1/2}$ for *t*BA homopolymerization with different macromonomer concentrations is estimated. Furthermore, the glass transition temperature and the thermal stability of these copolymers are studied by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. As an example, a transformation into an amphiphilic graft copolymer by corresponding hydrolysis of its precursor poly(*tert*-butyl acrylate-*g*-polystyrene) is presented.

2. Experimental

2.1. Materials

Macromonomer SR-4500 (ARCO Chemical Company), a poly(styrene) carrying a methacryloyloxy group at the chain end with a number-average molecular weight of 13,000 g/mol and $M_w/M_n = 1.05$, was used as received. 2,2′-Azobis(isobutyronitrile), AIBN, (Fluka) was purified by successive crystallizations from methanol. Benzene (Merck) and *tert*-butyl acrylate (*t*BA), (Merck) were purified by conventional methods [14].

2.2. Graft copolymer

The copolymer reactions were conducted in benzene solution using 8.0×10^{-3} mol/l of AIBN as initiator at 70 °C. Feed compositions consisted of a *t*BA monomer concentration of 1.5 mol/l and variable amounts of macromonomer. The reactions were followed by conventional dilatometric technique to attain limit conversion. Conversions of *t*BA were calculated from dilatometric data, since the low molar concentration of macromonomer in the mixture compared with that of *t*BA practically has no influence on the volume shrinkage of the system. The resulting polymer solutions were precipitated into methanol/water (1:1). The polymers were dried under vacuum at 40 °C, until a constant weight was reached.

The molecular weight distributions were measured by size exclusion chromatography (SEC) using a chromatographic system (Waters Division Millipore) equipped with a Waters Model 410 refractive index detector. Tetrahydrofuran, THF, (Scharlau) was used as eluant at a flow rate of 1 cm^3/min operated at 35 °C. Styragel packed columns; HR1, HR3, HR4E and HR5E were used. Poly(*tert*-butyl acrylate-*g*-polystyrene) graft copolymers were analyzed based upon 14 narrow-distribution standards of poly(methyl methacrylate), pMMA, (Polymer Laboratories) in the range between 1.4×10^6 and 3.0×10^3 g/mol.

2.3. Glass transition temperatures

Glass transition temperatures were measured using a differential scanning calorimeter, Perkin–Elmer DSC/TA7DX, PC series with liquid nitrogen. The temperature scale was calibrated from the melting point of high purity chemicals (lauric and stearic acids and indium). Samples (~10 mg) were weighed and quenched from room temperature at the maximum cooling rate to 0 °C and then scanned at 10 °C/min from 0 to 140 °C under dry nitrogen (20 cm^3/min). Three subsequent scans were performed at 10 °C/min for each sample. There was no waiting time between runs and the cooling rate was 10 °C/min.

The actual value for the glass transition temperature, T_g, was estimated as the temperature at the midpoint of the line drawn between the temperature of intersection of the initial tangent with the tangent drawn through the point of inflection of the trace and the temperature of intersection of the tangent drawn through the point of inflection with the final tangent. The current value is the average for several measurements realized for each composition.

2.4. Thermal degradation

A Perkin–Elmer TGA-7 instrument was used for the thermogravimetric measurements. The instrument was calibrated both for temperature and weight by the usual methods. Non-isothermal experiments were performed in the temperature range from 30–700 °C at heating rate of 10 °C/min. The average sample size was 6 mg and the dry nitrogen flow rate was 20 cm^3/min.

2.5. Hydrolysis

Polymer was dissolved in an equal weight of dioxane (based on the mass of polymer added), and a threefold excess of concentrated HCl was added (based on the moles of ester groups presented). The flask was covered with a condenser, and the solution was heated to reflux. After 6 h, the solution was cooled down, precipitated into hexane and then dried under vacuum to constant weight. The copolymer characterization was made using KBr pellets in a FT-IR Perkin–Elmer Spectrum One.

3. Results and discussion

The copolymer reactions were conducted in benzene solution using 8.0×10^{-3} mol/l of AIBN as initiator at 70 °C. The different amounts of macromonomer introduced on *t*BA monomer concentration of 1.5 mol/l as well as the yield obtained in the reactions are collected in Table 1.

The conversion of *t*BA to polymer was determined by

Table 1
Characteristics of *tert*-butyl acrylate polymerization in presence of polystyrene macromonomer in benzene solution and 8.0×10^{-3} mol/l of AIBN as initiator at 70 °C

Polymer	(Macrom.) 10^2 (g/cm^3)	Yield (%)	$k_p/k_t^{1/2}$ (mol$^{1/2}$ s$^{1/2}$ l$^{-1/2}$)
P*t*BA	0	92.0	1.76
P*t*BAS-1	1.30	92.7	1.40
P*t*BAS-2	2.62	88.3	1.27
P*t*BAS-3	4.31	92.9	1.17
P*t*BAS-4	5.21	92.4	1.15
P*t*BAS-5	7.80	95.9	0.98
P*t*BAS-6	10.41	91.8	0.93
P*t*BAS-7	15.61	94.8	0.99
P*t*BAS-8	20.81	93.0	1.06

measuring the ratio $\Delta V/\Delta V_\infty$, where ΔV and ΔV_∞ are the changes in volume at defined times and at conversion limit, respectively. Some of the curves obtained are depicted in Fig. 1. Considering a simple kinetic scheme, which includes a first-order decomposition of initiator, addition of primary radical to monomer, propagation and termination reactions, the variation of conversion, x, with time is given by:

$$\ln\frac{1}{1-x} = 2\frac{k_p}{k_t^{1/2}}\left(\frac{f[I]}{k_d}\right)^{1/2}[1 - \exp(-k_d t/2)] \qquad (1)$$

where k_p and k_t are the rate constant of propagation and termination, respectively; k_d is the rate coefficient of initiator decomposition, $[I]$ is the initiator concentration, f is efficiency factor and t is the time. It is suggested that the initiator efficiency is a function of the monomer type and the concentration [15], decreasing the efficiency as viscosity of the polymerization medium increases [16,17]. However, there is no available information in the literature about exact f values for this system. Therefore, and as a general accordance, a constant value of $f = 0.6$ is taking in this work. The value of k_d is estimated at 70 °C from the literature data [17–19], which is 3.69×10^{-5} s^{-1}. The experimental data were fitted to an exponential function and the attained $k_p/k_t^{1/2}$ values are collected in Table 1. The ratio between propagation and termination coefficients slightly decreases as macromonomer concentration increases up to a value from that it starts to increase. Variations of $k_p/k_t^{1/2}$ at different macromonomer concentrations are beyond the experimental error and should be attributed to changes in one or both rate coefficients. It is well known that propagation rate coefficient decreases when the growing radicals are trapped in a glassy matrix and the diffusion rate of monomer limits the propagation reaction [20–22]. Consequently, a decrease of propagation rate coefficient in our experimental conditions can be ruled out. It has been suggested [23,24] that the real value of k_t for a macroradical is controlled by its center of mass diffusion. Then, changes in the size of macroradicals or/and viscosity variations in the reaction medium produce a considerable modification in the diffusion-controlled termination rate. The presence of macromonomer into the reaction medium changes the thermodynamic quality of the solvent and, as O'Driscoll stated [25], any reduction in the solvent quality will cause the coil to shrink. In the smaller coil the chain end will be found easily by other chain end, k_t will be larger and therefore, $k_p/k_t^{1/2}$ will decrease.

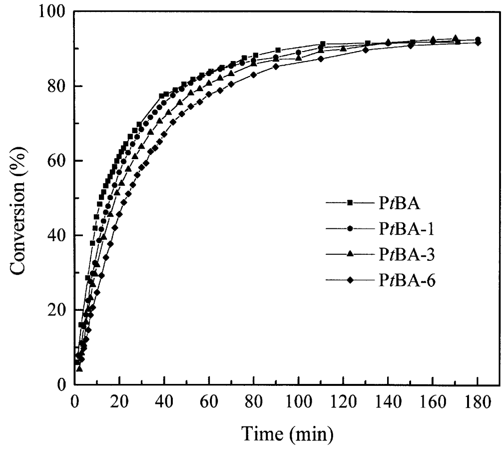


Fig. 1. Conversion versus time of various P(*t*BA-*g*-PS) graft copolymerizations.

Ludwico and Rosen [26] have observed that dissolved polystyrene or polybutadiene reduce the overall polymerization rate of styrene. Likewise, it has been described in simple bulk homopolymerizations that the overall polymerization rate decreases as a function of conversion before the onset of the gel effect [27]. A similar trend has been observed in the butyl acrylate polymerization in presence of the macromonomer used in this work [28]. In all the cases, the minimum has been attributed to the effect of dissolved polymer on the coil size of the terminating polymer radicals [23,25].

The subsequent increase of the lumped parameter $k_p/k_t^{1/2}$ might be interpreted as a change in the nature of the diffusion process, which is the rate-controlling step in the termination process.

A rough indication of this change has been previously reported [28]. A change of slope is produced at 9.3×10^{-3} g/cm^3 measuring the viscosities of macromonomer solution in benzene as a function of macromonomer. This crossover has been interpreted as a modification from dilute regime to semidilute solution. This change implicates an overlap of the coil and the loss of molecules individuality, which produces a lower value for k_t and consequently, an increase for $k_p/k_t^{1/2}$.

The graft copolymers were characterized by SEC. Fig. 2 depicts the size exclusion chromatograms of poly(*tert*-butyl acrylate) and various poly(*tert*-butyl acrylate-*g*-polystyrene) graft copolymers. It can be observed that the graft copolymer molecular weight increases as the macromonomer concentration in the feed does. It can be also noticed that a fraction of macromonomer is not incorporated into the graft copolymer. Different solvents and mixtures were used to achieve the separation, however, all of the attempts

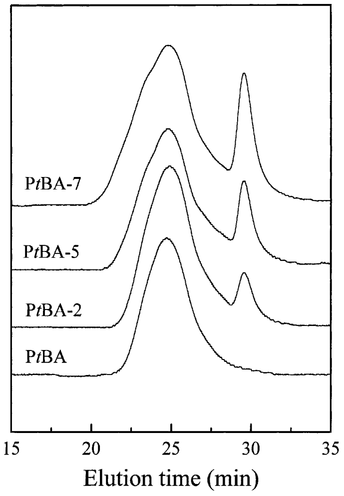


Fig. 2. Size exclusion chromatograms of PtBA and various P(tBA-g-PS) graft copolymers.

were unsuccessful. The enveloped curve has been deconvoluted into two individual curves, the first one describes the graft copolymers contribution whereas the second one is the macromonomer unreacted contribution. This deconvolution permits the evaluation of molecular weight average, although it is well documented that the absolute molecular weight of graft copolymers is difficult to assess by conventional static methods because of their branched structure and chemical composition heterogeneity. In Table 2 the unreacted macromonomer weight percentages regarding the macromonomer weight percentage introduced in the global feed are collected.

The average number of graft chains per backbone chain, N_{graft}, was calculated by using the following equations proposed by Capek et al. [29],

$$\bar{M}_{\mathrm{w}}^{\mathrm{total}} - \bar{M}_{\mathrm{w}}^{\mathrm{P}t\mathrm{BA}} = \sum \bar{M}_{\mathrm{w}}^{\mathrm{P}t\mathrm{BA}\text{-}g\text{-}\mathrm{PS}}$$

and

$$N_{\mathrm{graft}} = \sum \bar{M}_{\mathrm{w}}^{\mathrm{P}t\mathrm{BA}\text{-}g\text{-}\mathrm{PS}} / \bar{M}_{\mathrm{w}}^{\mathrm{PS}}$$

where $\bar{M}_{\mathrm{w}}^{\mathrm{total}}$ is the apparent weight-average molecular weight of graft copolymer, $\bar{M}_{\mathrm{w}}^{\mathrm{P}t\mathrm{BA}}$ is the apparent weight-average molecular weight of PtBA, obtained in absence of macromonomer, both determined by SEC. $\sum \bar{M}_{\mathrm{w}}^{\mathrm{P}t\mathrm{BA}\text{-}g\text{-}\mathrm{PS}}$ is an estimated apparent weight-average molecular weight of all grafted PS chains and $\bar{M}_{\mathrm{w}}^{\mathrm{PS}}$ is the apparent weight-average molecular weight of polystyrene macromonomer. The variations of the apparent weight-average and number-average molecular weight with the macromonomer concentration introduced in the feed are compiled in Table 2. These values increase as macromonomer concentration does and therefore, the amount of macromonomer incorporated into the graft copolymer and the number of grafts per chain increases. At this point, it is taken into account that SEC separation mechanism is based on the effective hydrodynamic volume of macromolecules rather than on their molecular weight. Therefore, application of this method to copolymer systems heterogeneous in composition and architecture is complicated because of on overlap of similar molecular sizes of various topology and composition [30]. Accordingly, the number of graft is approximated and should be taken with caution.

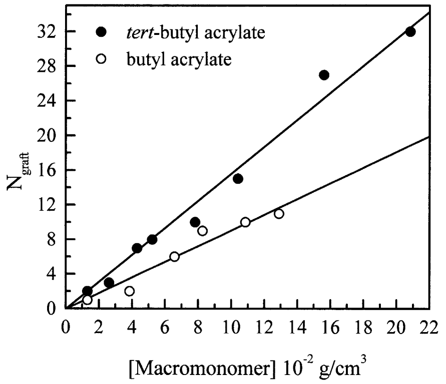


Fig. 3. Number of graft as a function of macromonomer concentration.

In a previous work [31], butyl acrylate has been polymerized with the same PS macromonomer and in similar experimental conditions. The number of PS graft introduced in the main chain has been determined [31]. These values along with those obtained for poly(*tert*-butyl acrylate-*g*-polystyrene) copolymerization are displayed in Fig. 3. As seen in both cases, the number of graft increases as macromonomer

Table 2
Some characteristics of the polymer samples obtained in the free radical polymerization of *tert*-butyl acrylate in presence of polystyrene macromonomer in benzene solution and 8.0×10^{-3} mol/l of AIBN as initiator at 70 °C

Polymer	Macrom. (%)	Macrom. residual (%)	$\bar{M}_{\mathrm{n}}$	$\bar{M}_{\mathrm{w}}$	N_{graft}
PtBA	0	–	148,000	379,000	–
PtBAS-1	6.4	6.1	152,000	405,000	2
PtBAS-2	12.0	7.5	155,000	418,000	3
PtBAS-3	18.3	8.8	175,000	465,000	7
PtBAS-4	21.3	11.2	177,000	491,000	8
PtBAS-5	28.9	11.3	170,000	509,000	10
PtBAS-6	35.1	17.1	178,000	569,000	15
PtBAS-7	44.9	17.2	181,000	738,000	27
PtBAS-8	52.0	17.0	204,000	797,000	32

Table 3
Number of graft, glass transition temperature, temperature of 5% mass loss, $T_{5\%}$, temperature of the first maximum, T_{max1}, and area percentages of the first maximum corresponding to each polymer

Polymer	N_{graft}	T_g (°C)	$T_{5\%}$ (°C)	T_{max1} (°C)	$\mathrm{Area}_{\mathrm{max1}}$ (%)
P*t*BA	–	48.4	255	262	51
P*t*BAS-1	2	49.7	257	262	45
P*t*BAS-2	3	51.1	259	271	42
P*t*BAS-3	7	50.6	261	272	40
P*t*BAS-4	8	50.7	257	273	39
P*t*BAS-5	10	50.6	258	269	35
P*t*BAS-6	15	53.3	261	267	32
P*t*BAS-7	27	53.5/95.7	260	268	28
P*t*BAS-8	32	55.0/96.6	266	276	26
Macromonomer	–	98.4	387	–	–

amount in the feed does. Bearing in mind that the chain end of macromonomer is a methacryloyloxy group end, we consider the following reported values of monomer reactivity ratios for both systems ($r_{\mathrm{MMA}} = 2.063$, $r_{\mathrm{BA}} = 0.349$ [32] and $r_{\mathrm{MMA}} = 1.61$, $r_{t\mathrm{BA}} = 0.66$ [33]). From this statement, the number of graft should be higher in the case of BA polymerization. However, and surprisingly, the number of graft is higher when *t*BA is polymerized. This feature might be related to the behavior of BA and *t*BA homopolymerizations, especially at high conversions and at temperatures above 30 °C. When BA polymerizes, a great number of side reactions, such as, intra e intermolecular chain transfer to polymer, chain transfer to monomer, etc. are occurring, which leads to changes in skeletal structure [10,34,35]. Thus, these secondary reactions could significantly affect the course of copolymerization in the case of butyl acrylate. This assumption may be considered with caution, since other alkyl acrylates might produce chain transfer reaction as BA does, though it is still unknown.

DSC measurements were carried out to discern the behavior of phase separation on the graft copolymer. In Table 3 are collected the glass transition temperatures of graft copolymers. A single glass transition temperature is detected in the DSC thermograms except for copolymers prepared with high macromonomer concentrations. Such a transition is slightly moved toward higher temperatures in the graft copolymers compared to the poly(*tert*-butyl acrylate). This shift is expected since the introduction of the rigid polystyrene macromonomer as a segment in the *t*BA structure would increase the T_g value. For copolymers prepared with high concentrations of macromonomer, a second transition at the T_g range of macromonomer is detected. To assure whether or not the T_g displacement correspond to the grafting in the copolymer, a blend of P*t*BA and macromonomer in a ratio of 50% w/w was prepared. The DSC trace showed two different glass transitions, one at 48 °C corresponding to poly(*tert*-butyl acrylate) and other at 97 °C corresponding to polystyrene macromonomer. It is important to remark that this macromonomer concentration in the blend does not alter the glass transition temperature of poly(*tert*-butyl acrylate).

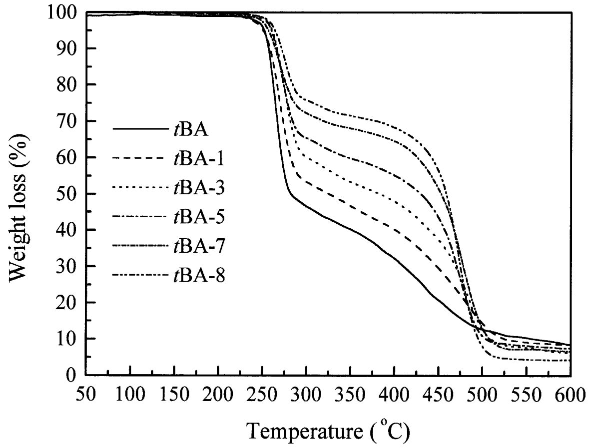
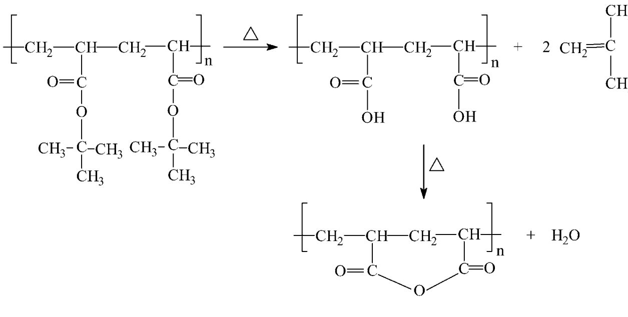


Fig. 4. The degradation curves under nitrogen at the heating rate 10 °C/min of P*t*BA and various P(*t*BA-*g*-PS) graft copolymers.

The TGA curves of the different copolymers as well as P*t*BA under nitrogen at 10 °C/min are shown in Fig. 4. As it is well established [34] the decomposition of P*t*BA is produced in two stages, the first one consists of the initial elimination of *tert*-butyl group given nearly quantitative yields of alkene per acrylate unit. The produced carboxylic acid groups dehydrate to give six-member cyclic anhydride structure and some water, as shown in the Scheme 1. The experimental data are quantitatively consistent with those reported in the literature [36]. The decomposition of polystyrene macromonomer is produced in a single sharp stage with a T_{max} at 426.0 °C. In the graft copolymers degradation two clear stages of degradation also appear: the first one is associated with the first stage of the degradation reaction in the backbone of the graft copolymer by similitude with the P*t*BA degradation. The second stage is attributed to the degradation reaction by either the chain scission in the branches or the random scission of the backbone.

The thermogravimetric behavior of a polymer depends on its structure and the type of substituents in the main chain. Therefore, a detailed analysis of first degradation peak can give information about the influence of the branches in the different solid-state properties.

The temperatures of 5% mass loss, $T_{5\%}$, and the maximum rate temperature of weight loss, T_{max}, corresponding to the



Scheme 1. Mechanism of the first stage of poly(*tert*-butyl acrylate) thermal degradation.

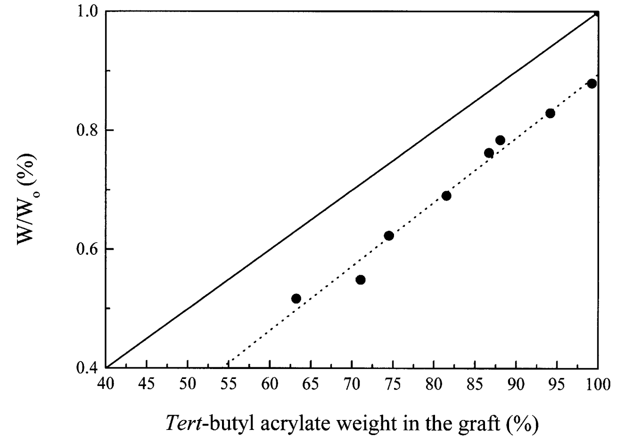


Fig. 5. The ratio between the percentage of weight loss of the degradation first stage in the graft copolymers, *W*, and the corresponding to the P*t*BA, W_o, as a function of *tert*-butyl acrylate weight in the copolymer.

first stage are collected in Table 3. The 5% weight loss temperature has been taken for simplicity as an index to assess thermal stability. A slight increase in the $T_{5\%}$ value and in the temperature of the first maximum in thermal degradation are found as the number of graft raises.

On the other hand, the introduction of PS in the chain decreases the weight loss of the first stage, which might be an indication that a PS unit located between two *t*BA units is stabilized relative to a *tert*-butyl acrylate triad. The ratio between the percentage of weight loss of the first stage degradation of the graft copolymer, *W*, and the corresponding of the homopolymer, W_o, as a function of *t*BA weight percentage in the copolymer is represented in Fig. 5. The difference between the solid line, corresponding to ideal mixture of P*t*BA and PS macromonomer, and the line drawn with the experimental data demonstrates the influence of branching in the degradation.

One of the goals of this work is to convert graft copolymers into amphiphilic materials by simple chemical reactions. Fig. 6 shows the FT-IR spectra of the graft copolymer with the highest number of branches (P*t*BAS-8) before and after hydrolysis. The peaks observed between 2800 and 3200 cm^{-1} are due to both the PS side chains and the P*t*BA backbone. After hydrolysis, the acid functionality is clearly visible as the broad absorbance from 2800 to 3800 cm^{-1}, and the carbonyl stretch has slightly shifted, as expected. The doublet band at ~1400 cm^{-1} corresponding to the stretching vibration of $-CH_3$ groups totally disappears after hydrolysis, which confirms that the precursor leads to an amphiphilic graft copolymer.

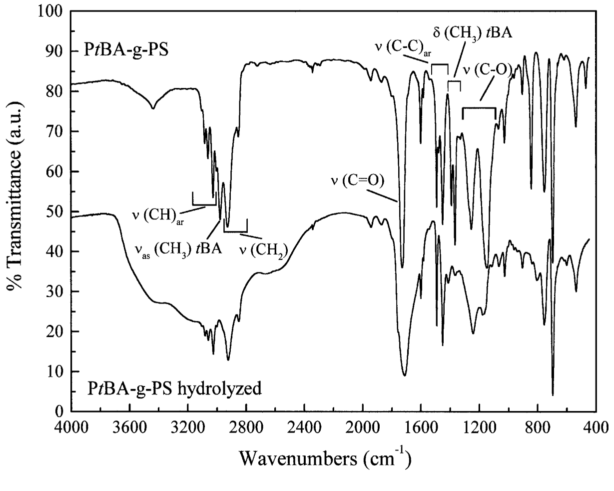


Fig. 6. FT-IR spectra of P*t*BAS-8 before and after hydrolysis.

4. Conclusions

Graft copolymers of polystyrene with *t*BA are successfully prepared by free radical copolymerization. The lumped rate constant $k_p/k_t^{1/2}$ for *t*BA solution polymerizations is dependent on the amount of macromonomer in the reaction medium. At the beginning $k_p/k_t^{1/2}$ decreases as macromonomer concentration increases, reaching a minimum value from that it starts to increase. The number of graft increases linearly as macromonomer concentration does. The grafts are responsible of the slight increase in the glass transition temperature as well as the thermal stability.

The synthesis of an amphiphilic graft copolymer, consisting of a hydrophilic poly(acrylic acid) backbone and hydrophobic poly(styrene) branches, is achieved by hydrolysis of the ester group of the *t*BA units in the backbone.

Acknowledgements

This research has been supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT), (MAT2000-1008). Dr M. Fernández-García and Dr M.L. Cerrada are grateful to the Comunidad Autónoma de Madrid and Ministerio de Educación y Cultura, respectively, for their financial support.

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