Characterization and Thermal Properties of Poly(*n*-butyl acrylate-*g*-styrene) Graft Copolymers

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ABSTRACT: Poly(butyl acrylate-*g*-styrene) graft copolymers were prepared by free-radical polymerization using a polystyrene macromonomer carrying a methacryloyloxy group at the chain end and they were characterized by size-exclusion chromatography, and Fourier transform infrared spectroscopy. Glass transition temperatures and degradation behavior were determined by thermal analysis. Only a single glass transition temperature was observed for the resulting graft copolymers, indicating the miscibility between the poly(styrene) phase and poly(butyl acrylate) (pBA) phase in the graft copolymer. The incorporation of polystyrene segments in the graft copolymer improved the thermal stability of pBA and enhanced the apparent activation energy for the thermal degradation of pBA. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 783–789, 2001

Key words: poly(butyl acrylate-*g*-styrene) graft copolymers; size-exclusion chromatography; Fourier transform infrared spectroscopy; glass transition temperature; thermal stability

INTRODUCTION

Block and graft copolymers have been extensively studied and have industrial applications, including surfactants, compatibilization agents in polymer blends, adhesives, additives in high-impact materials, and thermoplastic elastomers.[1] A special application for acrylic polymers, although relatively recently introduced, is the pressure-sensitive adhesives.[2,3] These adhesives are really viscous polymers, so the polymers must be used at temperatures above their glass transition temperature (T_g) values to permit the rapid flow. The adhesives flow because of the application of pressure; when the pressure is removed, the viscosity of the polymer is high enough to retain its adhesion to the surface. Many pressure-sensitive adhesives are used in all types of tapes, labels, decals, packaging, electrical insulation, and surgical bandaging.[4] They consist of permanently sticky or tacky polymer-based formulations usually coated onto rigid, relative to the adhesive, backings, which adhere spontaneously on contact with very little pressure to a variety of dissimilar surfaces without the use of solvent or heat.

There are three different methods to prepare block and graft copolymers—by using polymeric and multifunctional initiators, by modification reactions, or by using macromonomers. The macromonomer technique for graft polymer has received considerable attention recently. The advantage of the macromonomer method is that the number and length of the grafted branches can be controlled easily.[5] This type of copolymer has the potential to exhibit a wide variety of new physical and chemical characteristics, depending on the combination of polymer segments chosen.

It is well known that the thermal properties depend on their structure and the type of substituents in the main chain.[6] Hence, it is important to analyze the polymer thermal behavior to know the manufacturing temperature and the maximum temperature at which a given polymer is capable of operating for a extended period of time while still maintaining usable properties; in general, the applicability. In this regard, important efforts have been made in the determination of the T_g and the thermal stability of these copolymers. Besides, a common characteristic of the majority of multicomponent amorphous block and graft polymer systems in the solid state is their ability to exhibit microphase-separated structures.[7] Therefore, the phase behavior of the obtained block and graft copolymers has been studied by using differential scanning calorimetry (DSC), which gives information on the morphology depending on the existence and the position of the glass transition.[8]

This article describes the characterization by size-exclusion chromatography (SEC) and Fourier transform infrared spectroscopy (FTIR) of poly(butyl acrylate-g-styrene) [p(BA-g-S)] graft copolymers by using polystyrene macromonomer. The thermal properties, T_g and the thermal stability of these copolymers, have been studied by using DSC and thermogravimetric analysis, respectively. To investigate the effect of poly(styrene) (pS) content on thermal stability of poly(butyl acrylate) (pBA) segments, the decomposition of p(BA-g-S) was investigated by thermogravimetric analysis. The values of the apparent activation energy (E_a) for BA segments in thermal degradation were obtained by using the Horowitz-Metzger method.[9] The resulting E_a was compared with that for pBA.

EXPERIMENTAL

Materials

Macromonomer 4500, a pS carrying a methacryloyloxy group at the chain end with a number-average molecular weight of 13,000 g · mol^{-1}, from Arco Chemical Iberica, Barcelona, Spain (S.A.) was used in the present work. 2,2'-Azobisisobutyronitrile (AIBN) (Fluka) was purified by crystallization from methanol. Benzene (Merck) and n-butyl acrylate (BA) (Merck) were purified by conventional methods.[10]

Graft Copolymer

The copolymer reactions were conducted at 60°C in benzene solution using $2.0 \cdot 10^{-2}$ mol/L of AIBN as initiator. Feed compositions consisted of a butyl acrylate monomer concentration of 1.46 mol/L and variable amounts of macromonomer. The reactions were followed by conventional dilatometric technique until limit conversion was attained. Conversions of BA were calculated from dilatometric data, because the low concentration of macromonomer in the mixture has practically no influence on the volume shrinkage of the system.

The molecular weight distributions were measured by SEC by using a chromatographic system (Waters Division Millipore) equipped with a Waters Model 410 refractive index detector. Tetrahydrofuran (Scharlau) was used as eluant at a flow rate of 1 cm^3/min operated at 35°C. Styragel packed columns, HR1, HR4E, and HR5E were used. p(BA-g-S) graft copolymers were analyzed based on 14 narrow-distribution standards of polymethyl methacrylate (Polymer Laboratories) in the range between $1.4 \cdot 10^6$ and $3.0 \cdot 10^3$ g · mol^{-1} and known Mark-Houwink coefficients.[11] To elucidate the changes in the polymer for introduction of polystyrene, FTIR was used. The FTIR spectra were recorded from 4000 to 600 cm^{-1} using a Nicolet 520 FTIR Spectrometer.

T_gs

T_gs 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 to ±0.002 mg with an electronic autobalance (Perkin-Elmer AD4) and quenched from room temperature at the maximum cooling rate (−320 deg/min) to −80°C and then scanned at 10 deg/min from −80°C to 140°C under dry nitrogen (20 cm^3/min). Three subsequent scans were performed at 10 deg/min for each sample. There was no waiting time between runs and the cooling rate was 10 deg/min.

The actual value for the 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. The values estimated according to this criterion, when

Table I   Characteristics of Butyl Acrylate Polymerization in the Presence of Polystyrene Macromonomer at 60°C in Benzene Solution and 2.0 · 10^{-2} mol/L of AIBN as Initiator

Polymer	Macromonomer (%)	Yield (%)	Macromonomer Residual (%)	Macromonomer Reacted (%)	$\bar{M}_n$	$\bar{M}_w$	N_{graft}
Butyl acrylate	—	91.0	—	—	106,800	241,400	—
SBA-60-1	6.5	84.2	3.3	3.2	108,300	252,700	1
SBA-60-2	17.0	91.5	11.0	6.0	111,800	271,000	2
SBA-60-3	25.9	84.2	11.4	14.5	135,900	321,200	6
SBA-60-4	31.6	83.9	13.4	18.2	152,700	360,500	9
SBA-60-5	36.7	81.4	13.5	23.2	158,700	370,300	10
SBA-60-6	40.1	82.3	13.4	26.7	164,900	383,600	11

they are compared with those obtained following other procedures, might be apparently higher. In our case, this is also due in part to the heating rate used (10 deg/min).

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. Nonisothermal experiments were performed in the temperature range 30–700°C at heating rate of 10 deg/min. The average sample size was 4 mg and the dry nitrogen flow rate was 20 cm^3/min.

RESULTS AND DISCUSSION

The copolymer reactions were conducted at 60°C in benzene solution using 2.0 · 10^{-2} mol/L of AIBN as initiator. The different amounts of macromonomer introduced on butyl acrylate monomer concentration of 1.46 mol/L as well as the yield obtained in the reaction are shown in Table I.

The graft copolymers were characterized by means of SEC and FTIR spectroscopy. Figure 1 shows the size-exclusion chromatograms of polystyrene macromonomer, pBA, and various p(BA-*g*-S) graft copolymers. It can be seen that the graft copolymer molecular weight increases as the macromonomer concentration in the feed increases. It can also be seen that part of the unreacted macromonomer is always present in the graft copolymer. Nevertheless, attempts to separate any residual macromonomer from the graft copolymer by extraction with different solvents have been unsuccessful. The enveloped curve has been deconvoluted in two individual curves; the first one

describes the graft copolymers contribution whereas the second one is the macromonomer unreacted contribution. First, this deconvolution
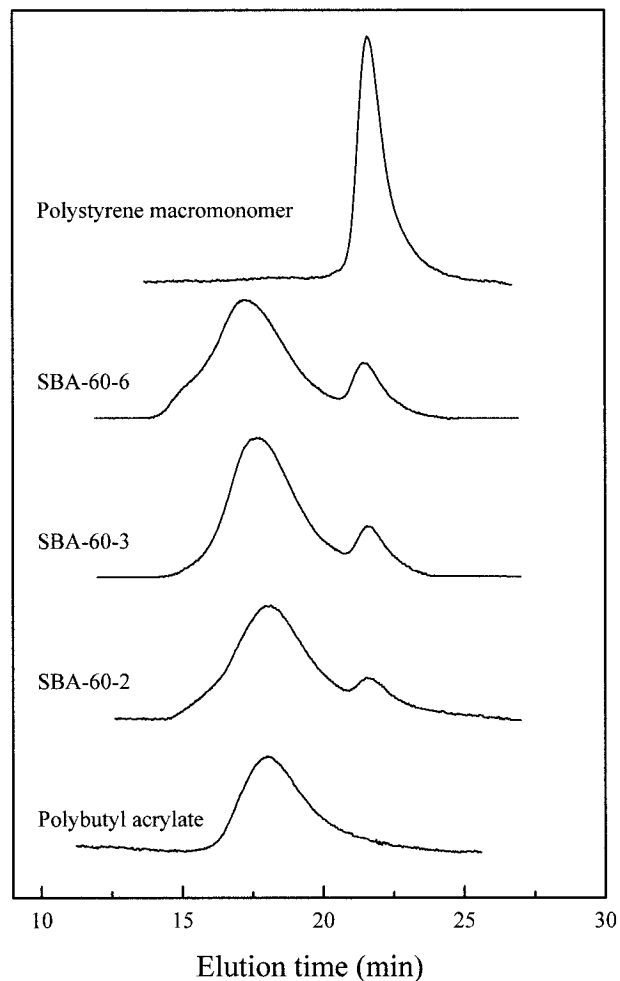

Figure 1   Size-exclusion chromatograms of polystyrene macromonomer, polybutyl acrylate, and various p(BA-*g*-S) graft copolymers.

permits the evaluation of molecular weight average, although it is well known 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 this work, it is assumed that the estimation of the graft molecular weight by application of the butyl acrylate Mark-Houwink coefficients[11] does not introduce massive errors. Second, it permits the determination of the residual or unreacted macromonomer amount. In Table I is compiled the residual and reacted macromonomer percentages in relation to the macromonomer percentage introduced in the global feed. It is important to mention that, in general terms, in all copolymerizations, the unreacted monomer has similar percentages, which could indicate that part of pS macromonomer has not been modified at the chain end with a methacryloyloxy group.

Capek et al.[12] calculated the average number of graft chains per backbone chain, N_{graft}, using the following equations proposed:

$$\bar{M}_w^{total} - \bar{M}_w^{PBA} = \sum \bar{M}_w^{PS\text{-}g\text{-}BA}$$

and

$$N_{graft} = \sum \bar{M}_w^{PS\text{-}g\text{-}BA}/\bar{M}_w^{PS}$$

where $\bar{M}_w^{total}$ is the apparent weight-average molecular weight of graft copolymer determined by SEC, $\bar{M}_w^{PBA}$ is the apparent weight-average molecular weight of PBA, obtained in absence of macromonomer, also determined by SEC, $\sum \bar{M}_w^{PS\text{-}g\text{-}BA}$ is an estimated apparent weight-average molecular weight of all grafted pS chains, and $\bar{M}_w^{PS}$ is the apparent weight-average molecular weight of polystyrene macromonomer. There are other methods to determine the number of grafts based on the M_n; however, M_w is chosen to calculate the number of grafts instead of M_n because as Heuts et al.[13] have shown, M_n is very sensitive to the baseline fluctuations, whereas M_w is less sensitive because M_w is more dependent on the high molecular weight end of the distribution, which is better defined. The variations of the apparent weight-average and number-average molecular weights with the macromonomer concentration introduced in the feed are summarized in Table I. These indicate that increasing the concentration of macroinitiator increases the averages. There-
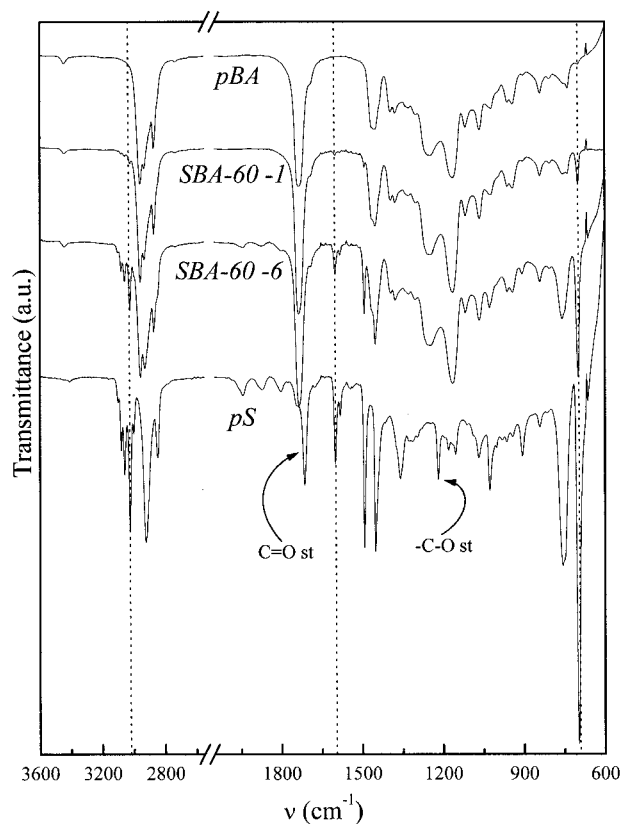

Figure 2   Infrared spectra of polystyrene macromonomer, polybutyl acrylate, and various p(BA-*g*-S) graft copolymers.

fore, the number of graft chains increase as the concentration of macromonomer increases. Regarding this, it is taken into account that SEC separation mechanism is based on the effective hydrodynamic volume of macromolecules rather than on their molecular weight. So, 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.[14]

The characteristic bands of pS macromonomer and pBA are observed in FTIR spectra showed in Figure 2. In the FTIR spectra of pS are shown the characteristic bands in the range of 3150–3000 cm^{-1} corresponding to the stretching vibration of arC—H, at 1600–1585 cm^{-1} corresponding to the doublet stretching vibration of arC—C, and at 760–700 cm^{-1} corresponding to the doublet rocking out of plane vibration of arC—H. Besides, the characteristic bands produced by the presence of methacryloyloxy group at the chain end can also be observed, such as the carbonyl absorption at 1715 cm^{-1} and —C—O stretching band at 1220

Table II   Number of Grafts, T_gs, Temperatures of 5% Mass Loss, $T_{5\%}$, Temperatures of the Maximums, T_{max1} and T_{max2}, Area Percentage of the Second Maximum, and the Apparent Activation Energy (E_a) Corresponding to Each Polymer

Polymer	N_{graft}	T_g (°C)	$T_{5\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	Area$_{max2}$ (%)	E_a (kJ/mol)
Butyl acrylate	—	−41.5	323.0	407.4	—	—	132
SBA-60-1	1	−41.3	321.8	406.7	439.5	3.1	143
SBA-60-2	2	−38.5	325.5	405.8	434.8	7.1	134
SBA-60-3	6	−36.7	351.0	408.8	439.4	17.6	173
SBA-60-4	9	−35.5	341.2	408.8	438.9	18.3	149
SBA-60-5	10	−33.8	348.0	407.1	436.2	26.6	165
SBA-60-6	11	−32.2	344.0	410.1	437.4	25.0	156
Macromonomer	—	98.4	386.9	—	426.0	—	297

cm^{-1}, marked in the figure. The growing of different bands corresponding to the pS in the graft copolymer spectra indicates the introduction of hard segment in the polymer. However, the difference between the grafted and unreacted macromonomer could not be attainable, because the characteristic bands are wrapped up in the global spectra.

DSC measurements were performed to know the behavior of phase separation on the graft copolymer. In Table II are collected the T_g of graft copolymers. Only a single transition is detected in the DSC thermograms for all copolymers and no transition at the T_g range of macromonomer (~98°C), which possibly indicates that the copolymer does not present phase separation. This would suggest that the unreacted macromonomer, the pS branches, and the backbone are miscible. Moreover, the T_g of the butyl acrylate shows a slight increasing compared with the pBA. Apparently with the introduction of the rigid polystyrene macromonomer as a segment in the butyl acrylate structure, an increasing of T_g is expected. This behavior has also been observed by Cheun et al.[15] on the free-radical copolymerization in benzene/dimethyl sulfoxide solution of methacrylate-terminated polystyrene with butyl acrylate. Figure 3 shows almost a linear relationship between the T_g of graft copolymers and the number of graft chains. To assure that the butyl acrylate displacement on its T_g is due to the introduction of branched pS in its structure, a blend of butyl acrylate and the macromonomer is measured with a macromonomer content of 40%. The DSC trace shows two different glass transitions, one at −41°C corresponding to butyl acrylate and another at 97°C corresponding to styrene macromonomer. It is noticeable that the introduction

of macromonomer in the blend does not alter the T_g of the butyl acrylate.

The TGA curves of the different copolymers under nitrogen at 10°C/min are shown in Figure 4(a). In Table II is represented the temperature of 5% mass loss, $T_{5\%}$. The 5% weight loss temperature has been taken for simplicity as an index to assess thermal stability. As shown in Table II, as the content of branching increases, the value of $T_{5\%}$ in thermal degradation increases. The differential thermogravimetric (DTG) curves, obtained from the original TGA are drawn in Figure 4(b). The maximum rate temperature of weight loss, T_{max}, corresponding to the degradation regions and the area percentage of the second maximum, are presented in Table II.

As can be seen in its DTG curve [Fig. 4(b)], the decomposition of pBA is produced in a broad single step with a maximum rate temperature of
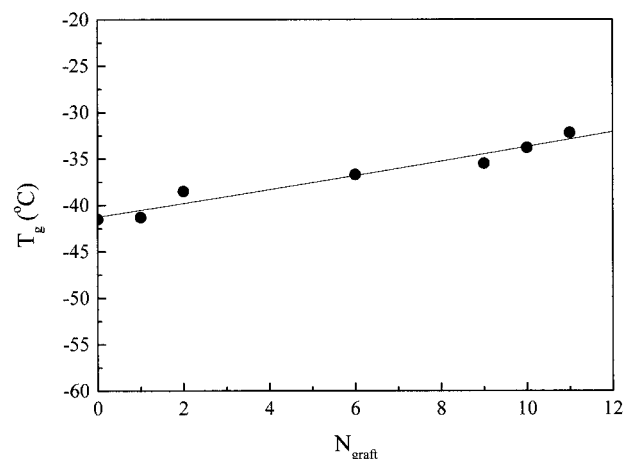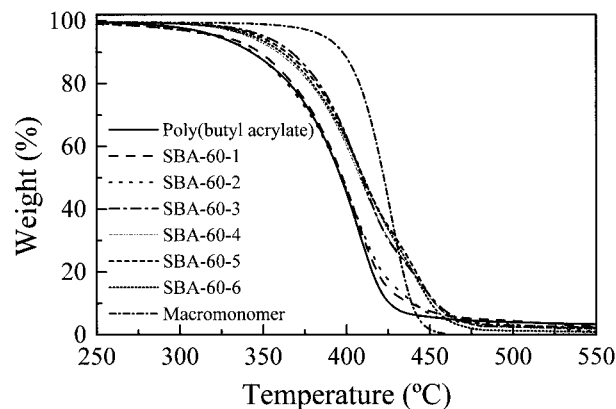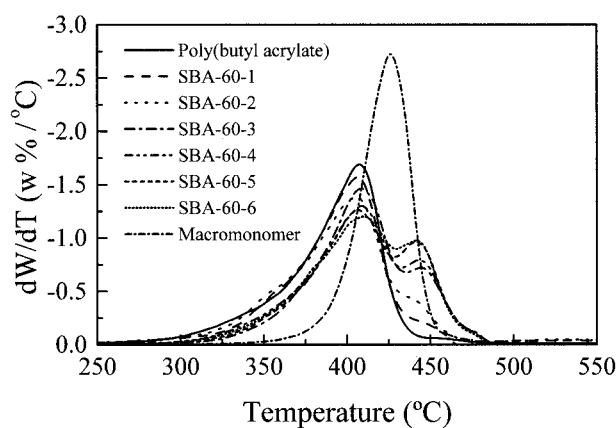

Figure 3 T_g of graft copolymers as a function of grafting.

(a)

(b)

Figure 4   (a) The degradation curves under nitrogen at the heating rate of 10°C/min for the graft copolymers and both homopolymers, and (b) the DTG curves.

weight loss at 407.4°C, whereas that in the decomposition of styrene macromonomer is produced by a sharp step with a T_{max} at 426.0°C. Because of the macromonomer monodispersity, the degradation develops homogeneously. In the graft copolymers, degradation appears at two decomposition maximums. The first one at ~410°C, is associated with the degradation reaction by random chain scission in the backbone of the graft copolymer because of its similitude with the pBA degradation. The second maximum, in the range of 440°C, is attributed to the degradation reaction by the chain scission in the branches. It is important to remark that the two T_{max}s are higher than that of the homopolymers independently of the pS content in the graft. Therefore, when pS is grafted, a higher stability of the main chain is achieved. The DTG curves are deconvoluted in

modified Gaussian curves and assuming a linear background over the temperature range of the fit. The area percentage of the second peak increases as the macromonomer content increases, and its values are in concordance with the percentage obtained for the reacted macromonomer (compare Tables I and II).

Having in mind that $T_{5\%}$ and the area percentage of the second peak vary with the pS content, it would be expected that the E_a for the pBA segment would be higher than that in pBA. The E_a of the thermal degradation for graft copolymers are calculated from the thermal degradation curves, using the Horowitz and Metzger[9] method, and assuming that the order of reaction is the unit, as shown in the following equation:

$$\ln\left[\ln\left(\frac{w_0}{w_T}\right)\right] = \frac{E_a\theta}{RT_{max}^2}$$

where w_o is the initial weight of polymer and w_T is the residual weight of polymer at temperature T, and θ is $T - T_{max}$. The activation energies are obtained from the slope E_a/RT_{max}^2 of the plot of $\ln[\ln(w_o/w_T)]$ versus θ for the main stage of the thermal degradation, as shown in Figure 5. In
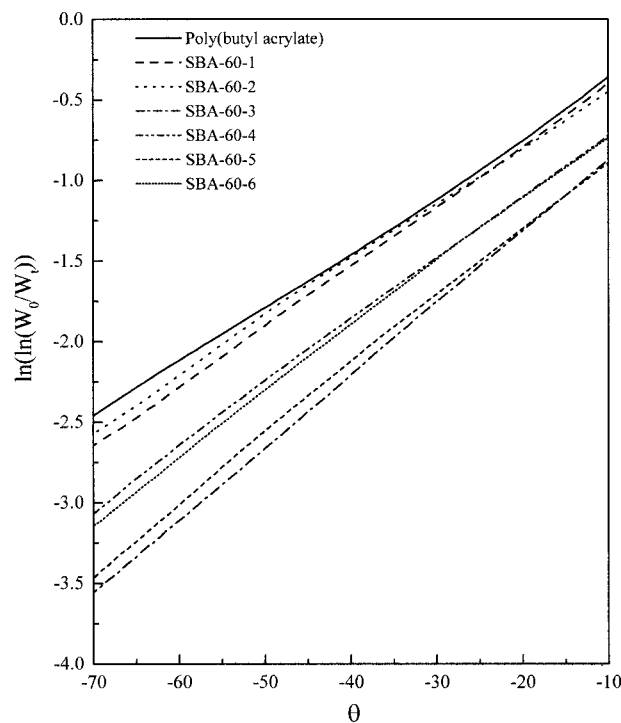

Figure 5   Plot of $\ln[\ln(w_o/w_T)]$ versus θ for thermal degradation under nitrogen at a heating rate 10°C/min of pBA and graft copolymers.

this case, the first stage corresponding to the degradation of the main chain is chosen to calculate the E_a. A good straight line is found for each copolymer in the range of temperatures from 330°C to T_{max}. The E_as for the thermal degradation of the graft copolymer increase as macromonomer content increases (Table II). This again indicates that the introduction of polystyrene macromonomer in the structure gives higher stability in the graft copolymer.

CONCLUSIONS

Copolymerizations of pBA with polystyrene containing a methacryloyloxy group at the chain end in different combinations were not prepared. The structures of graft copolymers were confirmed by SEC and FTIR. There were not evidences of phase separation by DSC, although the increase of copolymer T_g in respect to that of pBA is a function of the number of pS branch. Polystyrene hard segments enhanced the thermal stability of pBA. The E_as evaluated by the Horowitz and Metzger method[9] for graft copolymers were higher than that in pBA. It shows that the thermal stability of pBA segments is improved by the incorporation of pS segments.

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