

Synthesis and Thermal Degradation of Poly(*n*-butylisocyanate) Modified by 1,3-Propanesultone

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ABSTRACT: Poly(*n*-butylisocyanates) were synthesized by anionic homopolymerization with the addition of sulfonate groups in the termination stage. Two types of functional polymers were obtained from different quantities of added 1,3-propanesultone (PrS). When a stoichiometric proportion of sultone is added, the reaction with poly(*n*-butylisocyanate) renders a mix of a nonfunctionalized (PBIC) and a telechelic polymer (PBICT). In the presence of an excess of PrS, the proportion of end-functionalized chains was higher, and a significant change in their thermal properties was observed. Polymers were characterized by FTIR and NMR, and measurements of intrinsic viscosity were made. Ther-

mal degradation of the polymers was studied under nitrogen atmosphere for various heating rates. The kinetic parameters such as the activation energy and the reaction order were determined by using Ozawa's method. Thermal degradation analyses showed that the degradation processes depend strongly on the concentration of functional groups. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3594–3601, 2003

Key words: poly(*n*-butylisocyanate); functionalization of polymers; solution properties; thermal properties; thermal decomposition

INTRODUCTION

Polymers terminated with various types of functional groups have attracted the attention of many researchers mainly because of the applications of these materials.¹ Terminal functional groups modify the properties of the polymeric chains and may be susceptible to transformation reactions used in the production of novel block copolymers.²

The poly(isocyanate) molecule has a rod-like helical structure.³ This molecule has been the subject of a great deal of studies intended to test theoretical models for rigid and semirigid chains.^{4–7} The anisotropic conformation of the molecule in solution provides unique opportunities to study the self-organizing properties of these systems such as the presence of crystalline structures in the liquid state.^{8–10} At a given concentration, lyotropic liquid crystalline structures are produced. However, their applications have been restricted because of low thermal stability. According to the current literature, the intramolecular cyclization with initiation at the ends is the dominant mechanism of thermal decomposition of poly(*n*-butylisocyanate).¹¹

Recently, functionalization reactions have been widely used to modify polymeric materials properties, improving the performance of such materials. The objective of this work in this regard includes the chain-end functionalization of poly(*n*-butylisocyanate) with a sulfonate group to increase the thermal stability of this polymer. In addition, an analysis of such reaction with charged groups is given, inasmuch as it may promote the modification of the ordered phases, which are very sensitive to the presence of terminal groups in the chain.

Elastomers terminated with ionic groups such as a carboxylates,¹² sulfonates,¹³ or phosphines¹⁴ have been the subject of numerous studies. These ionic telechelic polymers showed interesting viscoelastic and dielectric properties. However, lesser attention has been given to telechelic rigid or semirigid materials such as poly(isocyanates). Recently,^{15,16} there has been interest in the study of asymmetric molecules having a stable dipolar moment, for which several computer simulations have been carried out and experimental data are still lacking. In this regard, telechelic poly(*n*-butylisocyanates) may provide results to compare with theoretical predictions. Poly(isocyanates) have shown electrorheological properties,¹⁷ and the increase in the dipolar moment of the molecule by chemical modification may improve these properties.

This article presents the synthesis, characterization, and thermal degradation of poly(*n*-butylisocyanates), where the end group is a sulfonate group. A compar-

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ison of properties between functionalized and non-functional polymers is presented.

THEORY

Thermogravimetric (TGA) experiments for different heating rates $\beta = dT/dt$ allow the determination of the polymer degradation kinetic parameters. The conversion C at a constant temperature is defined as the relative loss of weight: $C = (w_0 - w)/w_0$, where w_0 and w represent the initial and the weight at time (t), respectively. The rate of chemical reaction can be expressed as a function of conversion C by the kinetic equation:

$$\frac{dC}{dt} = kf(C) \quad (1)$$

The rate of conversion depends on C according to the equation

$$f(C) = (1 - C)^n \quad (2)$$

where n is the order of reaction. These equations can be substituted into the Arrhenius equation to obtain

$$\frac{dC}{dt} = A(1 - C)^n e^{(E/RT)} \quad (3)$$

In TGA experiments, the rate of heating β is kept constant, and then eq. (3) can be written as

$$\frac{dC}{(1 - C)^n} = \frac{A}{\beta} e^{-(E/RT)} dT \quad (4)$$

The integration of eq. (4) was developed by Doyle¹⁸ and Ozawa,¹⁹ giving the following form:

$$-\log \beta_1 - 0.457 \frac{E_1}{RT_1} = -\log \beta_2 - 0.457 \frac{E_2}{RT_2} \quad (5)$$

where R is the universal constant of gases, T_1 and T_2 are absolute temperatures associated with the different heating rates β_1 and β_2 for the same weight loss.

The determination of order of reaction was obtained by using the relationship^{19,20} between C and n :

$$\log \beta = \begin{cases} \log[(1 - C)^{1-n} - 1] & \text{for } n \neq 1 \\ \log[\ln(1 - C)] & \text{for } n = 1 \end{cases} \quad (6)$$

EXPERIMENTAL

Materials

n-Butylisocyanate and 1,3-propanesultone (PrS) (Aldrich Chemical Co., USA) were used in the synthesis with *N,N*-dimethylformamide (DMF), carbon tetrachloride (CCl₄), and methanol (Baker Co., USA). All reagents (99% purity) were purified by degassing and vacuum distillation during the polymerization process. Sodium cyanide (Aldrich) was used as the initiator, previously activated by heating for 5 h at 423 K.

Polymerization conditions

Polymers were obtained by a method²¹ similar to the one reported by Shashoua.²² Polymerization was carried out in DMF at a temperature lower than 223 K, with sodium cyanide as initiator. An unfunctionalized poly(*n*-butylisocyanate), PBIC, and two end-capped functionalized telechelic polymers (PBICTs) were obtained. For the case of PBIC, methanol was added at the terminal stage of the reaction. Conditions of this polymerization were used as reference to obtain samples of PBICT1 and PBICT2, by modifying only the terminal stage by adding PrS instead of methanol. The first PBICT was obtained by functionalization under stoichiometric conditions (sample PBICT1). Stoichiometry was calculated on the basis of the molecular weight of PBIC, adding two molecules of PrS per each molecule of polymer. We assume 100% conversion. The other PBICT sample (PBICT2) was terminated with an excess of PrS to guarantee the highest degree of functionalization. The quantity of PrS added to this sample was 700 times higher than the one used under stoichiometric conditions. All samples were purified by dissolution in CCl₄, precipitation with methanol, and drying for 24 h at 313 K in vacuum. The resulting telechelic polymers were also washed with acetone to eliminate the excess of free PrS. Subsequently, the functionalized samples were cleaned with a mixture CCl₄/HCl (99 : 1) to eliminate the excess of PrS that could be interacting with the polymer molecule. These samples were named PBICT1C and PBICT2C. In all cases, polymers were not fractionated.

Characterization of polymers

Infrared spectra were obtained from thin polymer films (CCl₄) by using a Perkin-Elmer 1615 FTIR Spectrometer. NMR spectra of polymers were carried out in deuterated chloroform recorded at 298 K in a 500 MHz Bruker DMX500 spectrometer. Elemental Analysis was used to verify the chemical composition of

TABLE I
Conditions of Synthesis, Viscosity, and Molecular Weight of Synthesized Polymers

Sample	Initiator (g/dL)	PrS (g/dL)	[η] (mL/g)	M_n	Conv. (%)
PBIC	0.089	—	634	9.4×10^4	11.9
PBICT1	0.100	0.028	733	1.0×10^5 ^a	17.9
PBICT1C	0.100	0.028	725	1.0×10^5 ^a	17.9
PBICT2	0.091	20.8	2360	3.0×10^5 ^a	22.7
PBICT2C	0.091	20.8	2350	2.8×10^5 ^a	22.7

^a Apparent M_n because the synthesis conditions are very similar to the PBIC.

the polymers (Dessert Analytics, Tucson, AZ). The proportion of carbon, hydrogen, nitrogen, and sulfur was measured, and the oxygen content was obtained by a mass balance. The intrinsic viscosity was determined at 303 K in an Ubbelohde viscometer by using CCl_4 as solvent. The molecular weight of the unfunctionalized polymers was obtained by using the Mark-Houwink constants reported by Ambler et al.²³ for PBIC (see Table I). The M_n value for PBICT was obtained by comparison with that of the PBIC sample, synthesized at the same conditions. The contribution of functional end groups was not considered in this determination.

Thermal gravimetric analysis (TGA) was made in a DuPont thermobalance model 910 linked to a Thermal Analyzer 2100 microprocessor. The heating rate (β) was set to 1, 5, 10, 20, and 40°C/min; the size of samples was 4.8 ± 0.5 mg and all experiments were performed under nitrogen conditions by using a flow of 50 mL/min.

RESULTS AND DISCUSSION

Polymerization was carried out at an initiator concentration that guarantees a molecular weight below 10^6 Da. This favors the rod-like conformation of the molecules^{20,22} (see Table I). Under these conditions, the polymerization renders low yields, with monomer conversion between 11 and 23%.²³ Results of elemental analysis are shown in Table II, where the expected percentage of each element (theoretical) and the mea-

sured percentage (experimental) are reported. The last column gives the number of sulfur atoms per each polymer molecule. Data were calculated on the basis of the PBIC content. With regard to the sulfur content, one atom of sulfur was expected to appear per each molecule of PBICT. However, for the sample PBICT2, the sulfur content was abnormally high as compared to the main elements of the monomer (N, C, and H). The latter result indicates the possible presence of PrS aggregates with the polymer. When sample PBICT2 is washed with CCl_4/HCl (99 : 1), a product with considerable less sulfur is obtained (PBICT2C sample) and its properties are very similar to those of the original PBICT2. A polymer with one atom of sulfur per each molecule was obtained after a double-washing process, but the polymer was degraded as its NMR spectrum showed.

Results of the elemental analysis of PBICT1 render nine sulfur atoms per molecule, which indicates that some quantity of PrS is tied to the polymer. By washing the sample in a CCl_4/HCl solution, the sulfur content diminished to 1.8 sulfur atoms per polymer molecule (PBICT1C). With additional washing, an additional reduction to a constant value of 0.5 sulfur atoms per each polymer molecule results. These results confirmed the hypothesis that stoichiometric conditions are insufficient to give an entire functionalization of all PBIC molecules and hence, a mixture of PBIC and PBICT was obtained.

In all samples, infrared spectra show a strong absorption band at about 1700 cm^{-1} corresponding to the carbonyl group, and a broad band in $1280\text{--}1390\text{ cm}^{-1}$ corresponding to the disubstituted amide structure. Both bands are characteristic of poly(isocyanates).³ The spectra of the PBIC and of PBICT1 are very similar and correspond to spectra reported by Shashoua.²² It was not possible to detect the small quantity of terminal groups (NH , SO_3^-) by using this technique.

The FTIR spectrum of sample PBICT2 shows two additional bands at 1200 and 1040 cm^{-1} [Fig. 1(a)], which are characteristic for vibrations of asymmetric and symmetric stretching of SO_3^- groups. The existence of these groups in ionic form implies that the PrS undergoes a ring opening reaction (Scheme 1), but is

TABLE II
Elemental Analysis for Synthesized Polymers

	C (%)		H (%)		N (%)		O (%)		S (%)		No. S
	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	
PBIC	60.6	60.3	9.1	9.1	14.1	13.7	16.2	16.9	0.03	—	—
PBICT1		60.6		9.4		14.5		15.9		0.31	10
PBICT1C		60.7		8.8		12.3		18.2		0.06	1.8
PBICT2		53.6		8.5		12.1		22.5		3.30	97
PBICT2C		59.2		9.2		12.9		18.4		0.32	9.4

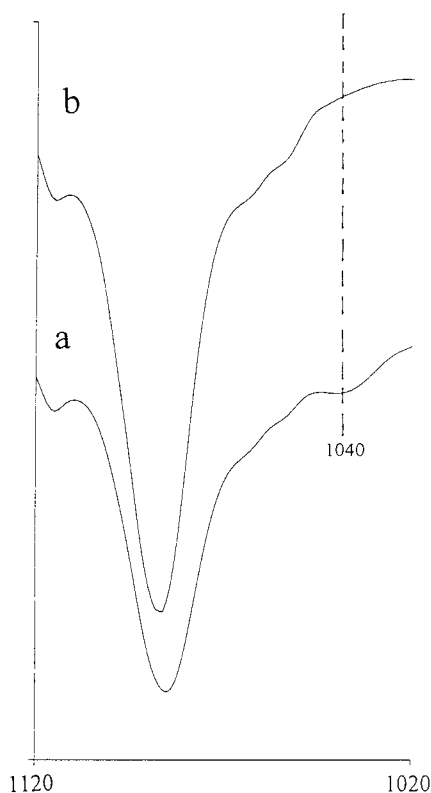
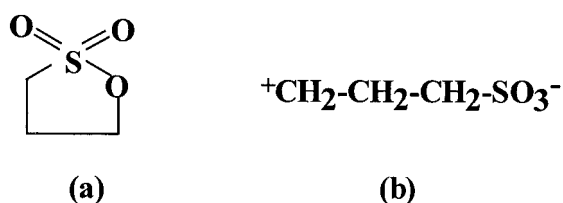


Figure 1 FTIR spectra for PBICT1 sample: (a) before, (b) after cleaning with CCl_4/HCl .

not able to homopolymerize, as was reported elsewhere.^{24,25} The generated SO_3^- groups present electrostatic interactions with the polymer molecule and remain attached to it, making cleaning difficult. A sample cleaned up with the CCl_4/HCl solution does not show the band at 1040 cm^{-1} [see Fig. 1(b)]. This means that the groups SO_3^- covalently attached to the polymer are not detectable by IR.

The $^1\text{H-NMR}$ spectrum of the PBIC presents signals corresponding to protons of butyl groups. The chemical shifts are 0.9 ppm for the $-\text{CH}_3$ group (A), 1.3 ppm (B), and 1.6 ppm (C) for the $-\text{CH}_2$ middle groups of butyl, and 3.9 ppm for $\text{N}-\text{CH}_2$ (D). In the stoichiometric functionalization, the quantity of propane sultone in the PBICT1 sample was small. This makes the detection of its protons by NMR very difficult, so the spectrum was the same as in PBIC. Figure



Scheme 1 1,3-propanesultone: (a) closed form, (b) zwitterionic open form.

2 shows the spectra of samples PBICT2 [Fig. 2(a)] and PBICT2C [Fig. 2(b)]. In the PBICT2 spectrum, detection of all the proton signals of the butyl group (A to D), and the new peaks (E to I), were assigned to the PrS aggregates and impurities. Therefore, the peak in Figure 2(a) (a triplet, G) at 3.1 ppm can be assigned to two methylene protons, $-\text{CH}_2-\text{SO}_3^-$; the peak at 2.1 (a quintuplet, I) belongs to two methylene protons, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_3^-$; the peak at 3.5 ppm (a triplet, E) belongs to two methylene protons, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_3^-$. Finally, the peak at 2.7 ppm [a triplet, H in Fig. 2(a)] is assigned to two methylene protons in the middle of PrS in the cycle. These new signals are not present in PBICT2C [see Fig. 2(b)]. This sample also shows a change in the shape of peak D corresponding to the isocyanate group, and this may be an indication of the beginning of the degradation. Assignments to all the peaks can be made by using the two-dimensional scalar-coupling chart generated by the COSY pulse sequence. Similar resonance values for PrS were reported for protons of PrS in sulfobetaines.²⁶

Viscosity measurements

Unfunctionalized PBIC has good solubility in carbon tetrachloride, benzene, and chloroform. It also shows partial solubility in toluene, and the functionalized PBIC shows a reduction of solubility in these solvents. It has been reported²³ that chloroform induces degradation of the polymer chain, and solutions in benzene⁸ need to be prepared at 313 K. Therefore, CCl_4 was chosen as solvent for viscosity measurements.

The intrinsic viscosity, $([\eta])$, of the polymer samples shows that the hydrodynamic properties depend

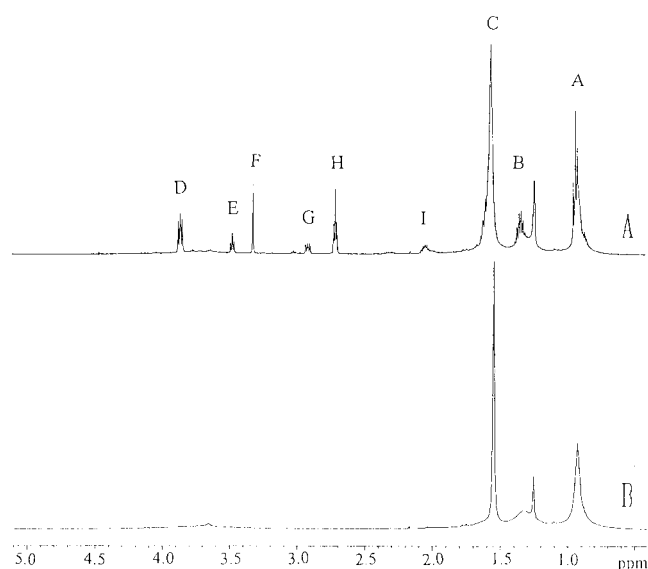


Figure 2 $^1\text{H-NMR}$ spectra of the samples: (a) PBICT2, (b) PBICT2C.

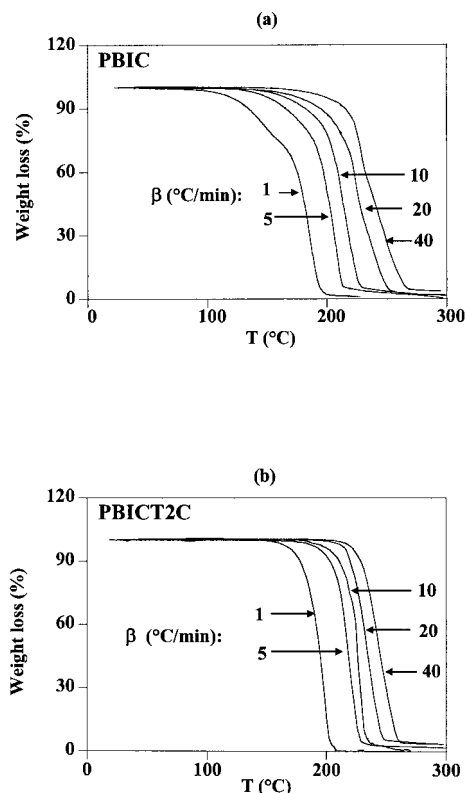


Figure 3 TGA curves of poly(isocyanates) at various heating rates in nitrogen atmosphere: (a) PBIC, (b) PBICT2C samples.

strongly on the presence of the sulfonate group.²⁷ Under similar conditions, the polymers containing PrS show a significant increase in the intrinsic viscosity values (see Table I). For the PBICT2, the solution concentration needed for the viscosity measurements is 10 times smaller than that of PBIC; therefore, the intrinsic viscosity obtained is higher in PBICT2, up to three times (30 times at the same concentration) that of the unfunctionalized PBIC sample. The PBICT2 sample shows open PrS aggregates, and after a second cleaning process sample PBICT2C was obtained. To determine the influence of these aggregates on the $[\eta]$ value, the viscosities of PBICT2 and cleaned sample (PBICT2C) were compared. The quantity of PrS aggregates is 10 times higher in sample PBICT2 than in PBICT2C. However, both samples show almost the same intrinsic viscosity $[\eta]$. This means that the presence of end groups of PrS in PBICT2 is the primary cause of the change in the viscosity, and the influence of PrS aggregates is not significant for the hydrodynamic properties of these polymers. According to the elemental analysis results, only a reduced part of the polymer chains in sample PBICT1 is functionalized. For this reason, the change in viscosity for PBICT1 is smaller than that observed in PBICT2. Indeed, only a 12% increase in intrinsic viscosity was observed in samples PBIC and PBICT1, which implies that the

amount of functionalized chains in the PBICT1 sample is small. Polymers PBICT1 and PBICT2C have similar proportions of PrS open groups. Differences in viscosity levels confirm the hypothesis that only the charges linked to the polymer chain by covalent bond affect the viscosity of samples. A portion of the polymer that precipitates at the end of the polymerization may be the reason for the large excess of PrS.

Thermal degradation

The temperature at which intensive degradation is initiated, T_i , at a given heating rate, was taken as a criterion of heat stability of the polymers. The initial size of each sample was almost the same, 5 ± 1 mg, which allows us to compare the initial decomposition temperature of various synthesized polymers. The TGA curves for thermal degradation of a sample of PBIC and PBICT2C are shown in Figure 3(a, b). The graphs clearly reveal the strong influence of the heating rates on thermal decomposition. When the heating rate is increased from 1 to 40 °C/min, an increase of 50 °C in the initial thermal decomposition temperature (T_i) is measured in both cases. The difference of the thermal behavior between functionalized and unfunctionalized polymers can be seen in Figure 4(a, b). These figures show the temperatures where the polymer samples have lost 5 and 50% of their initial weight, respectively, as a function of the heating rate

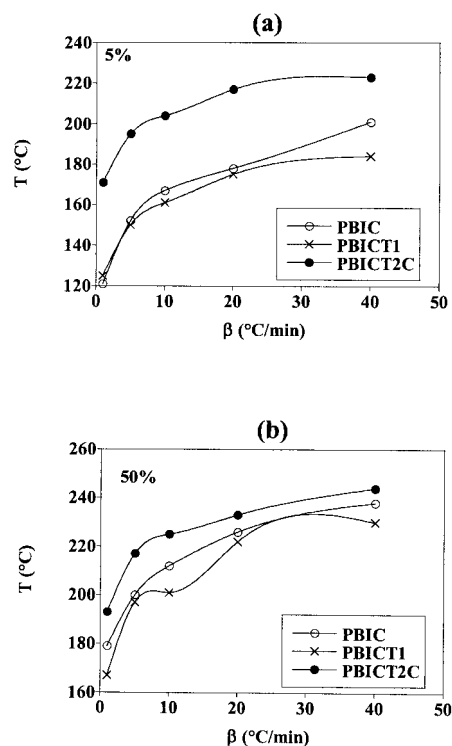


Figure 4 Decomposition temperatures of poly(isocyanate) for different heating rates: (a) 5% and (b) 50% of weight loss.

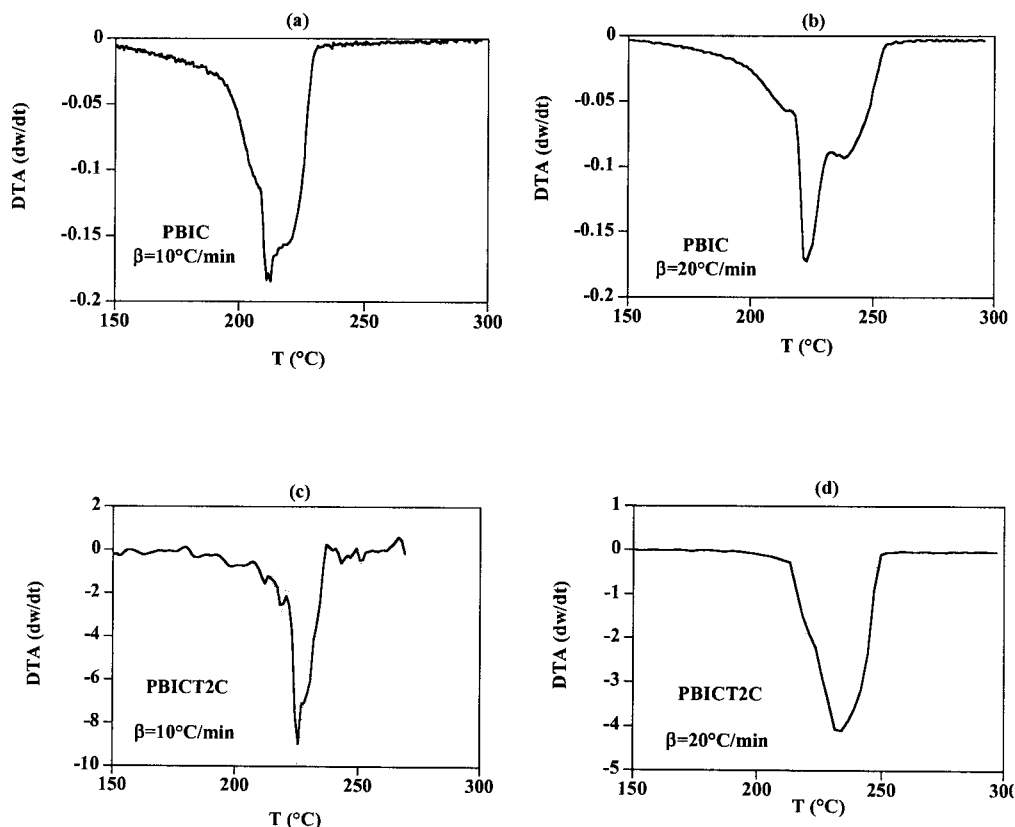


Figure 5 TGA derivative curves for PBIC and PBICT2C samples at different heating rates (a) and (c) at $\beta = 10^\circ\text{C}/\text{min}$; (b) and (d) at $\beta = 20^\circ\text{C}/\text{min}$.

(β). The decomposition behavior of the samples PBIC and PBICT1 is very similar in both graphs, because in this last sample the functionalization was not complete. However, sample PBICT2C, which has the highest degree of functionalization, shows an increase in thermal stability (50 and 10°C with 5 and 50% weight loss, respectively), at all heating rates. Therefore, from the above figures, it is shown that in the first stage of decomposition (5% wt loss) PBICT2C is more stable than during the second stage (50% wt loss) as compared with unfunctionalized PBIC. This observation may be explained in terms of the presence of the sulfonate end groups on the macromolecule.

Durairaj et al.¹¹ reported two stages of degradation for different alkyl isocyanate polymers. In our case, it is not easy to establish the different stages of degradation from the TGA curves of PBIC [see Fig. 3(a)]. To improve the understanding of these stages, the derivative dw/dT (where w is the weight) is plotted in Figure 5. For $\beta = 10^\circ\text{C}/\text{min}$, both processes occur at almost the same time [Fig. 5(a)], but for $\beta = 20^\circ\text{C}/\text{min}$, the first degradation process is terminated at a lower temperature [see Fig. 5(b)]. When the heating rate is slow ($\beta < 10^\circ\text{C}/\text{min}$), the stage of polymer decomposition begins at a lower temperature and occurs so slowly that only one stage of the degradation process

is seen. For the telechelic sample PBICT2C, only one degradation stage is observed [see Fig. 5(c, d)] at $\beta = 10$ and $\beta = 20^\circ\text{C}/\text{min}$.

Isothermal experiments confirm improvements in the thermal stability of the telechelic polymers as compared with the uncharged polymer. In Figure 6, the weight loss as a function of time in an isothermal process at 100°C is plotted. PBIC and PBICT1 samples begin decomposition at 5 min. The PBICT2C sample is stable up to 120 min, whereas PBIC exhibited a weight loss approximately two times higher than the partially

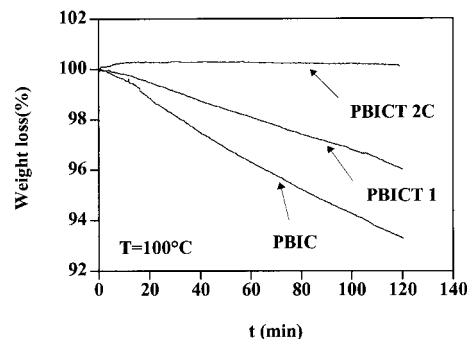


Figure 6 Decreasing of weight loss for poly(isocyanate) samples during isothermal process at 100°C .

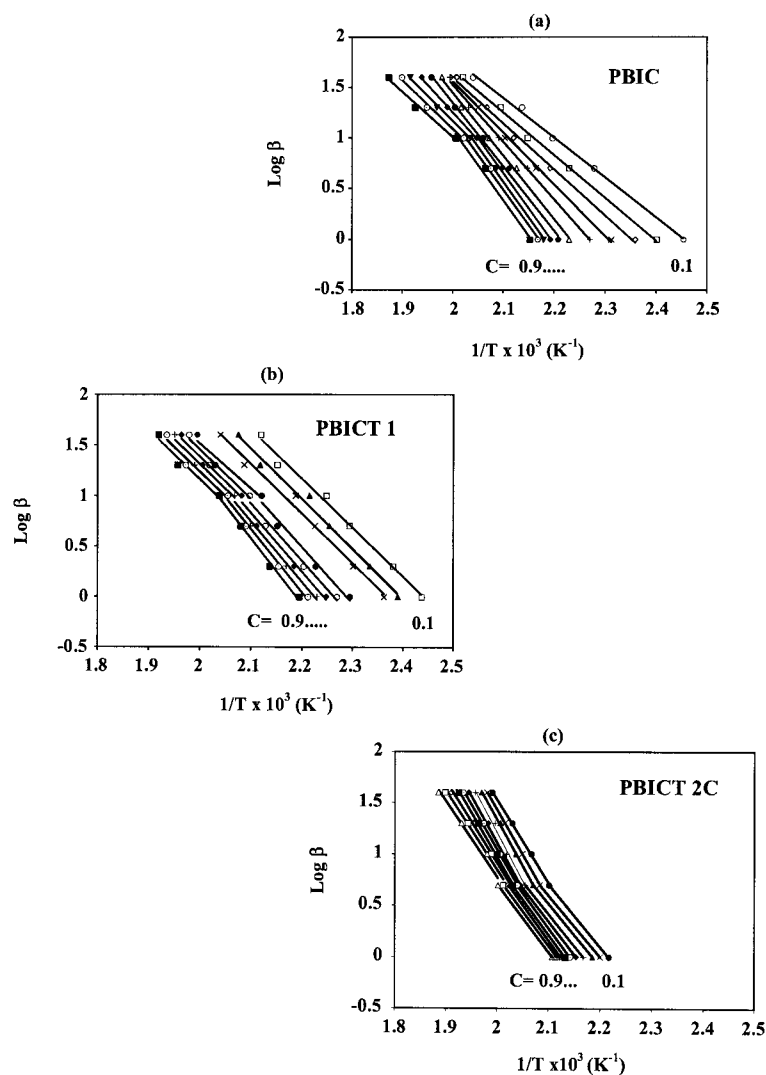


Figure 7 $\text{Log } \beta$ versus reciprocal absolute temperature for the Ozawa method for (a) PBIC, (b) PBICT1, (c) PBICT2C samples.

charged polymer (PBICT1). This means that under these conditions, only unfunctionalized chains of this sample are degraded.

To calculate the activation energy, Ozawa's method (see eq. 5) was used. Straight lines for various weight fractions ($C = 0.1$ – 0.9) are shown in Figure 7 for three polymers. In Figure 7(c), PBICT2C, data are restricted within a narrow temperature interval, in contrast to unfunctionalized PBIC [see Fig. 7(a)]. Data indicate an increase in the thermal stability of functionalized polymers, as compared to PBIC, during the degradation stages. This supports the conclusion that the terminal group induces an increase in the thermal stability of the polymer.

The thermal degradation of telechelic and unfunctionalized poly(*n*-butylisocyanates) is a very complex process, and therefore the reaction order of this system is not a meaningful parameter. Under low heating rate, a single maximum of the derivative of weight loss (Fig. 5) is apparent, from which it may be possible

to estimate an apparent order of the thermal degradation process for these samples. Figure 8 shows the plot of eq. (6) intended to obtain the reaction order for two samples. A good linear relationship is obtained for two samples (PBIC and PBICT1), which renders a reaction of order unity in both cases.

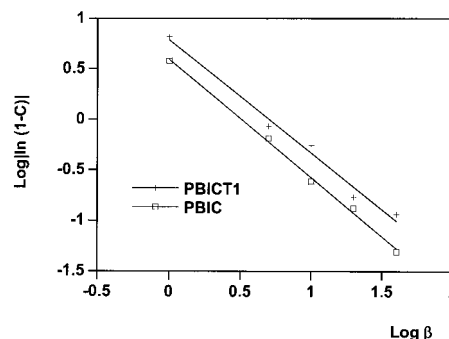


Figure 8 Relationship obtained by the Ozawa method for $n = 1$ (PBIC and PBICT1 samples).

CONCLUSION

Functionalized poly(isocyanates) were obtained by adding PrS at the final stage of the polymerization. An excess of PrS renders a higher degree of functionalization, but the purification of the polymer is difficult, because the standard method to eliminate the PrS excess produces degradation of the polymer. Functionalized polymers have viscosity values higher than those observed in the unfunctionalized polymer.

Thermal degradation of functionalized poly(*n*-butylisocyanate) is a complex process, which depends strongly on the heating rate or time of exposure to isothermal conditions. The experiments confirmed the influence of the terminal group on the thermal stability of the polymer. Functionalization of the polymer from a stoichiometric proportion of propanesultone did not affect their thermal properties, because not all the molecules were functionalized. The higher the degree of functionalization, the larger the increase in thermal stability of PBIC. The functionalized polymer represents a model chain of charged rods, whose properties are currently under investigation in this laboratory.

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