Viscoelastic Properties of Random Poly(butylene adipate/isophthalate) Copolymers

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ABSTRACT: The viscoelastic properties of random poly(butylene adipate/isophthalate) copolymers of various molecular weights and compositions were investigated by dynamic testing in the molten state. For all samples the storage and loss components of the dynamic shear modulus, $G'(\omega)$ and $G''(\omega)$, were measured at different temperatures. The zero-shear viscosity, η_0, for each composition was correlated to the weight-average molecular weight, M_w, by the equation: $\eta_0 = KM_w^a$ and the exponent a was found to increase as the content of isophthalate units was increased. Also, increases in the activation energy for viscous flow were observed as the isophthalate unit content was increased. The dynamic viscoelastic behavior of the copolymers was studied in terms of the complex compliances; curve fitting results on data of $J'(\omega)$ and $J''(\omega)$ vs. ω showed that such curves can be accurately reproduced by the following equation: $J^*(\omega) = J_g + (J_e^0 - J_g)/[1 + (i\omega\tau_2)^{\beta_2}] + i/\omega\eta_0$. It was concluded that, in the investigated frequency and temperature ranges, a single retardation phenomenon in the terminal zone provides a satisfactory description of the viscoelastic behavior of the copolymers. The values of the viscoelastic parameters were found to vary monotonically with composition, as expected in the case of statistical copolymers. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1213–1221, 1997

Key words: random copolymers; copolyesters; viscoelasticity; poly(butylene adipate); poly(butylene isophthalate)

INTRODUCTION

In recent years several types of copolyesters have been produced and employed in industrial applications and this fact has given a strong impulse to the study of the correlations between physical properties and copolyester structure. Thus, investigations on the various kinds of comonomeric units and their relative amount and disposition in the chains have been performed with the pur-

pose of designing synthetic processes leading to materials with a balanced combination of specific properties. The polymeric system investigated in this work was a series of random copolyesters of poly(butylene adipate) (PBA) and poly(butylene isophthalate) (PBIP). This kind of copolyester, poly(butylene adipate/isophthalate) (PBABIP), has been selected because the two constituent homopolymers are employed in a variety of industrial processes. Moreover, PBABIP samples display good solubility in common solvents, which facilitates their molecular characterization. Results of detailed investigations on the dilute solu-
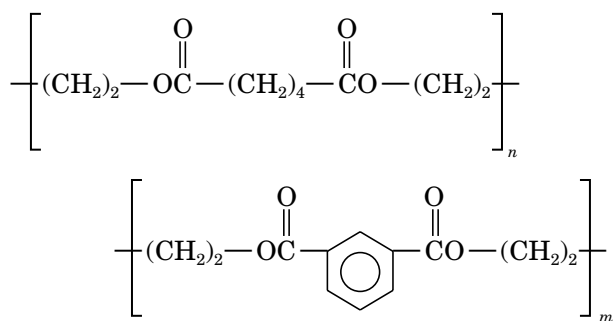
Scheme 1

tion[1] and thermal properties[2] of these copolymers have been previously reported.

The development of industrial applications of thermoplastic polymers requires the prior knowledge of their rheological behavior in different processing conditions. The storage and loss components, G' and G'', of the dynamic shear modulus can characterize, with the required accuracy, the viscoelasticity of polymers in the range of temperatures and deformation rates of practical industrial interest. The importance of both G' and G'' is due to the physical significance of these functions. In fact G' is directly related to the elastic energy which is recovered by the sample under test upon removal of the driving force for deformation, whereas G'' provides a measure of the energy loss stemming from the unrecoverable deformation due to the purely viscous flow of the sample. The present work focuses on the relationships between the viscoelastic parameters of the PBABIP copolymers and their composition, to define synthesis conditions leading to suitable materials for specific industrial applications.

EXPERIMENTAL

Synthesis of Polymer Samples

Samples of poly(butylene adipate/isophthalate) copolymers (Scheme 1) were synthesized in bulk by the usual two-stage polycondensation procedure,[1] starting from dimethyladipate (DMA), dimethylisophthalate (DMIP) and 1,4-butanediol (BD) and using $Ti(OBu)_4$ as catalyst. Due to the high temperature of the second stage (about 220°C) and to the presence of titanium tetrabutoxide, which favor the redistribution reactions, statistical copolyesters were expected.[1,3] The syntheses were carried out employing different ratios

DMIP/DMA (0, 20, 50, 80 mol % adipate), in order to obtain copolymers with different compositions. During each synthesis some samples were withdrawn from the reactor at different reaction times to produce polymers with the same composition and different molecular weights.

Molecular, Thermal and Dilute Solution Characterization

The number-average molecular weight, M_n, was determined using a Vapor Pressure Osmometer Wescan mod. 233; the thermal characteristics were analyzed by means of a Du Pont 9900 Thermal Analyzer; and the intrinsic viscosity in chloroform at 30°C was measured for all samples employing a viscometer of the Ubbelhode type. More details on these characterizations are reported elsewhere.[1,2] Relevant data are collected in Table I.

Rheological Measurements

Rheological measurements were performed with an Instron Rotary Rheometer mod. 3250, driven by a Solartron 1170 frequency generator-analyzer through an analog servo-loop. The cone-plate geometry was used for the whole set of dynamic measurements; cone angle was 7.5° and plate diameter 40 mm. Samples were prepared by molding the copolymer powders into homogeneous circular plates with diameters and thicknesses slightly larger than the dimensions of the cone-plate fixtures. The specimens were inserted on the top of the plate and the gap was adjusted by lowering the cone in small steps to allow complete relaxation of the compressive forces. Temperature at the plate was measured by an iron/constantan thermocouple attached by an isothermal junction to an HP3497A data acquisition/control unit. The temperature drop across the sample was corrected with the aid of a calibration curve obtained by preliminary measurements. A constant nitrogen flow was maintained in the heating chamber to avoid sample oxidative degradation. Frequency sweeps were performed in the range 0.01–100 Hz and the complex torque components, $T^*\sin \delta$ and $T^*\cos \delta$, were measured by the function analyzer. For each frequency, ν, the storage and loss dynamic moduli G' and G'' were computed by the following relationships:

$$G' = \frac{3T^*\beta}{2\pi\alpha r^3\sin \delta} \tag{1}$$

Table I   Molecular and Thermal Characterization Data

Sample Identification	Adipate (mol %)	$[\eta]^a$ (dL g^{-1})	$M_w \times 10^{-3b}$	$M_w/M_n{}^b$	$T_g{}^c$ (K)	$T_m{}^c$ (K)
80PBABIP2	80	0.355	9.98	1.96	225	322
80PBABIP3	80	0.402	11.6	1.97	225	324
80PBABIP4	80	0.580	19.2	1.98	225	322
50PBABIP2	50	0.372	12.0	1.97	244	339
50PBABIP3	50	0.515	17.5	1.98	250	340
20PBABIP2	20	0.337	11.0	1.96	272	394
20PBABIP3	20	0.527	18.8	1.98	276	392
20PBABIP4	20	0.670	23.2	1.98	277	390
PBIP	0	0.435	28.0	1.97	299	421

[a] In chloroform at 30°C.

[b] Calculated from experimental M_n values, assuming a random distribution of both molecular weights and composition. (See ref. 1.)

[c] From ref. 2.

$$G'' = \frac{3T^*\beta}{2\pi\alpha r^3\cos\ \delta} \qquad (2)$$

where β is the cone angle, α the imposed angular deformation, r the cone radius, and δ the loss angle. The corresponding values of the complex viscosities and compliances, η^* and J^*, and of their real and imaginary components, η', η'', J' and J'', were subsequently computed according to standard textbook relationships.[4a]

The absence of significative sample degradation was controlled by repeating some measurements at low frequencies. The temperature range for experiments was selected for each sample in such a way as to avoid both thermal degradation effects and the onset of crystallization or vitrification processes. For each sample a minimum of four frequency sweeps at different temperatures were performed to obtain reliable estimates of the activation energy for viscous flow, E_a.

RESULTS AND DISCUSSION

From the dynamic rheometer data, zero-shear viscosity, η_0, at different temperatures was estimated by plotting η' versus η''. The resulting circular arc plots (Cole–Cole plots),[5,6] can be described by the following equation:

$$\eta^* = \eta' - i\eta'' = \frac{\eta_0}{(1 + i\omega\tau_0)^{1-h}} \qquad (3)$$

where $\omega = 2\pi\nu$, h is a parameter related to the

eccentricity of the circular arc and τ_0 is a characteristic relaxation time.[5-7] The simple geometric relationships among the elements of the circular arcs reported in Figure 1 allow η'' to be expressed as a function of η' and of the parameters η_0 (the intersection of the circular arc with the real axis) and h. These two parameters can be obtained by linear least-squares fitting to the observed values of η' and η''. Figure 1 shows that $\eta''(\omega)$ attains a maximum in the investigated frequency range.
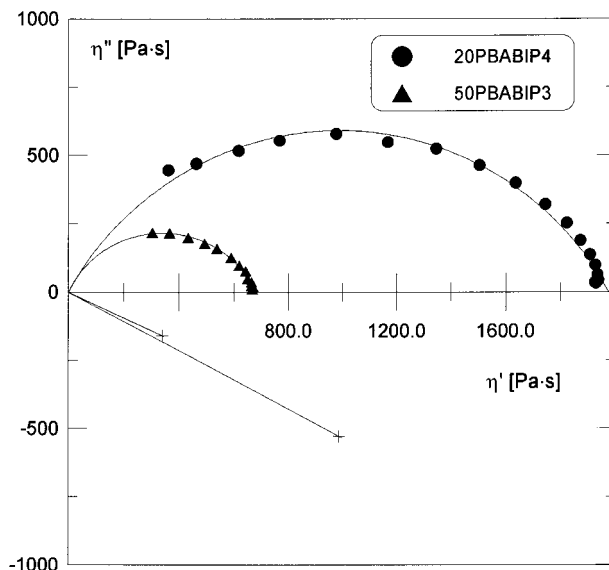
Figure 1   Cole-Cole plots of complex viscosity for samples 50PBABIP3 at $T = 91.5$°C and 20PBABIP4 at $T = 134.1$°C. The zero-shear viscosity η_0 is given as the intercept on the right-hand side of the circular arc with the η'-axis. The distances of the crosshairs from the η'-axis are given by $(\eta_0/2)\tan(h\pi/2)$. [See also eq. (3).]

Table II   Zero-Shear Viscosity at Different Temperatures

Sample Identification	T °C	η_0 Pa s	T °C	η_0 Pa s
80PBABIP2	62.5	127	69.1	88
	64.7	112	73.7	75
80PBABIP3	71.1	255	86.7	124
	81.3	159	93.9	92
80PBABIP4	86.0	433	98.5	241
	93.4	314	103.0	196
50PBABIP2	82.9	213	87.6	178
	85.0	180	91.3	140
50PBABIP3	91.5	679	99.6	433
	94.8	531	106.1	316
20PBABIP2	122.4	—	131.1	64
	124.4	83	135.1	55
20PBABIP3	130.5	693	142.7	397
	135.3	555	148.9	324
	139.2	479		
20PBABIP4	124.7	3303	146.5	1273
	134.1	1992	168.3	533
PBIP	155.6	302	164.5	191
	157.6	255	166.6	174
	160.1	232		

The value of ω corresponding to this maximum, ω_c, is then used to compute τ_0 ($\tau_0 = 1/\omega_c$).[5–7] Table II reports values of η_0 obtained by eq. (3). These values have been checked against values obtained by the following limit:

$$\eta_0 = \lim_{\omega \to 0} \left[\frac{G''(\omega)}{\omega} \right] \qquad (4)$$

For the samples investigated in this work, both methods give practically the same η_0 values.

The temperature dependence of η_0 was analyzed and an Arrhenius-type equation was found to fit satisfactorily the experimental data in the investigated temperature range:

$$\eta_{0,T} = A \exp\left(\frac{E_a}{RT} \right) \qquad (5)$$

where E_a is the activation energy for viscous flow, R is the universal gas constant and the temperature T is expressed in K. The values of E_a obtained by eq. (5) are collected in Table III and their dependence on copolymer composition is shown in Figure 2. Inspection of the figure and of the data in Table III shows that E_a increases as PBIP unit content is increased. According to the free volume theory, E_a is inversely proportional to f^2, where f is the fractional free volume of the polymeric system.[4b] Thus, results in Figure 2 suggest that f decreases as the isophthalate fraction in the copolymer is increased. Data in Figure 2 show also that for each copolymer, E_a increases as the molecular weight is increased, a trend which has been reported for several polymers.[4b] According to the free volume theory, this behavior can be attributed to the decrease in the relative amounts of chain free-ends as molecular weight is increased. Since the fractional free volume, f, is inversely proportional to the number-average molecular weight, M_n, and E_a scales with $1/f^2$, then, for each copolymer, the activation energy should be directly proportional to M_n^2.[4b] However, the low number of samples for each composition does not allow a significant testing of this correlation.

The dependence of η_0 on the weight-average molecular weight, M_w, has also been investigated. Equation (5) was used to compute, for each sample, the value of the zero-shear viscosity at a common reference temperature, $T_{\rm ref}$; the η_0 values at $T_{\rm ref}$ have been correlated to M_w by the relationship[8]

$$\eta_0 = KM_w^a \qquad (6)$$

Table III   Rheological Characterization Results

Sample Identification	E_a (kcal mol^{-1})	η_0[a] (Pa s)	$G_0 \times 10^{-5}$[a] (Pa)	$J_g \times 10^{6}$[a] (Pa^{-1})	$J_e^0 \times 10^{5}$[a] (Pa^{-1})	η''_{max}/η_0[a]
80PBABIP2	11.0	16.2	1.5	6.9	1.1	0.41
80PBABIP3	11.2	19.4	1.6	5.5	1.8	0.37
80PBABIP4	12.6	53.9	1.6	3.3	2.2	0.32
50PBABIP2	11.6	25.9	1.8	5.0	2.3	0.34
50PBABIP3	14.4	79.7	1.9	3.2	1.3	0.33
20PBABIP2	12.2	52.3	1.3	—	—	0.50
20PBABIP3	14.4	560	2.0	1.7	2.0	0.32
20PBABIP4	14.9	2043	2.0	1.5	1.5	0.30
PBIP	16.0	725	1.9	4.1	1.4	0.35

[a] At $T_{ref} = 135°C$.

The following values of a and K were obtained by a linear least-square analysis of the log–log plot:

$$a = 3.4 \quad K = 2.92 \times 10^{-12}$$
$$\text{for   80PBABIP   } T_{ref} = 75°C$$

$$a = 4.1 \quad K = 2.28 \times 10^{-15}$$
$$\text{for   50PBABIP   } T_{ref} = 90°C$$

$$a = 4.7 \quad K = 4.21 \times 10^{-18}$$
$$\text{for   20PBABIP   } T_{ref} = 135°C$$

$$a = 4.6 \quad K = 1.26 \times 10^{-19}$$
$$\text{for   PBIP   } T_{ref} = 200°C^{[9]}$$

From these data it appears that the exponent of M_w increases as the PBIP unit content is increased. The cross-correlation among η_0, M_w and temperature has been investigated to check whether the above-reported dependencies of η_0 on M_w change as the reference temperature is changed. Values of a in eq. (6) have been computed for several T_{ref}'s in the range 70–140°C. However, irrespective of the selected T_{ref}, such a trend was always confirmed: values of a increase as PBIP monomeric unit content in the copolymer is increased. In a previous paper on the rheological characteristics of the homopolymer PBIP[9] it has been reported that this exponent was about 4.6 at 200°C, a value well above the "universal" one of 3.4. This discrepancy was attributed to the presence in the homopolymer of a fraction of cyclic oligomers whose content was shown to decrease with increasing molecular weight. The plasticizing effect of these cyclic products can lead to substantial decreases of the viscosities of the low-

molecular-weight samples.[9] Values of a are correspondingly increased. An analogous deviation of the a exponent above the "universal" 3.4 value is detected for our PBABIP copolymers with the higher contents of PBIP units, suggesting that the effects of cyclic oligomers in the PBIP fraction may be responsible for this behavior.

Since the rheological measurements on PBABIP copolymers have been performed in different temperature ranges, the dependence of the viscoelastic properties on the temperature can affect the comparison among different samples. This dependence can be eliminated by the reduction of data to a common reference temperature, T_{ref}; according to the time-temperature superposition principle, curves of $G'(\omega)$ and $G''(\omega)$ versus ω obtained at different temperatures were shifted along the frequency axis to obtain a master curve at a given T_{ref}. Shift factors a_T were computed as
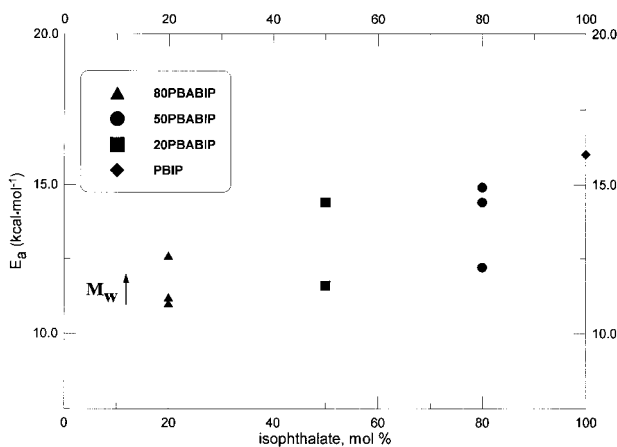
Figure 2   Effect of copolymer composition on the activation energy for viscous flow, E_a. (See text.)
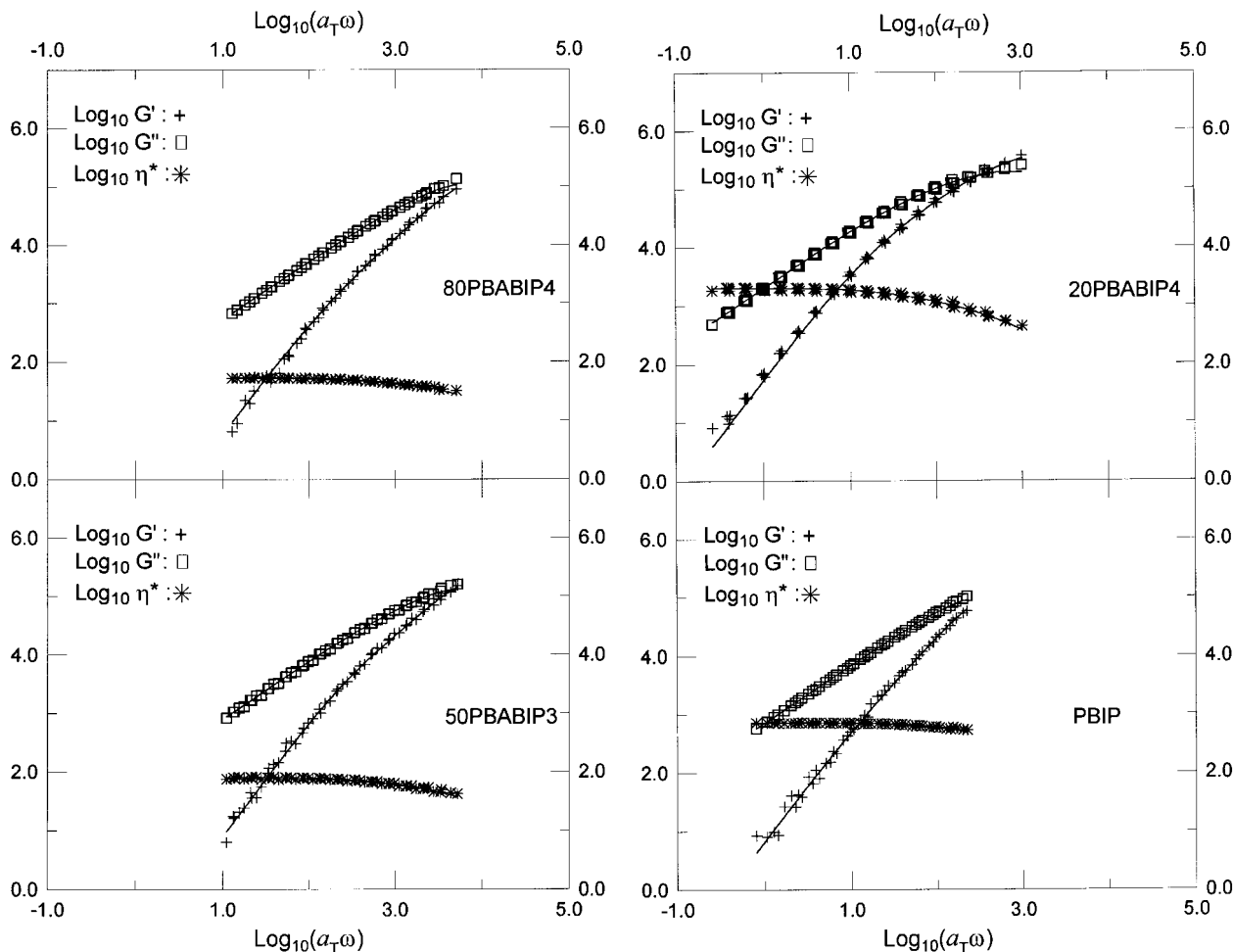
Figure 3 Master curves of storage modulus G', loss modulus G'' and of the magnitude of complex viscosity η^* for some representative copolymer samples. $T_{\text{ref}} = 135°C$. Solid lines have been drawn according to results of the best fit to eq. (8).

$$a_T = \frac{\eta_{0,T}}{\eta_{0,T_{\text{ref}}}} \qquad (7)$$

where $\eta_{0,T}$ values were calculated by eq. (5). No vertical shift corrections (of the Rouse type) were applied. Figure 3 reports the master curves for some representative samples at $T_{\text{ref}} = 135°C$.

Least squares analysis of complex viscosities η^* was performed by fitting values at $T_{\text{ref}} = 135°C$ to eq. (3). Values of η_0, τ_0 and h have been obtained for each copolymer sample. Table III reports the values of η_0 and $G_0 = \eta_0/\tau_0$, a parameter related to the elastic behavior of the polymer sample in the terminal zone.[7] Inspection of data in Table III shows that for each copolymer composition, a characteristic range of G_0-values can be identified. Moreover G_0 increases as the PBIP content in the copolymers is increased; this fact can

be related to the stiffening of the copolymeric chain due to increasing amounts of PBIP monomeric units.

The analysis of the viscoelastic properties can also provide information on the distribution of molecular weights (MWD). Correlations between MWD and viscoelastic functions were investigated by plotting the polydispersity index, $d = M_w/M_n$, vs. $(\eta_0/2\eta''_{\text{max}})^2$.[10] Cole–Cole plots (see Fig. 1) were used to estimate maximum values of the storage component of the complex viscosity, η''_{max}. Data reported in Table III and Figure 4 show that the average value of $(\eta_0/2\eta''_{\text{max}})^2$ is approximately 2. However, a deviation from the above ratio is observed for samples of low M_w, suggesting that the values of d reported in Table I may be affected by a systematic error. Polydispersity indexes have been computed with the as-
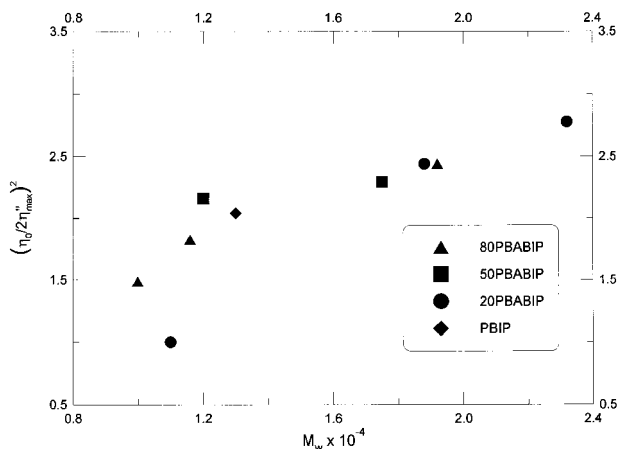
Figure 4 Dependence of the parameter $(\eta_0/2\eta''_{max})^2$ on the weight-average molecular weight M_w.

sumption that the used set of synthesis conditions led to the "most probable" MWD, which corresponds also to perfectly statistical copolymers. It has been shown that for long polymerization times this hypothesis can provide accurate estimates of the sample polydispersity.[3] Inspection of data in Figure 4 confirms that for $M_w > 12,000$ sample polydispersity is fairly constant, in agreement with the d-values in Table I. The situation with samples of lower M_w is different so that, in this case, also questions on the statistical arrangement of the co-monomeric units can be raised. However, for PBABIP samples of low M_w at high temperatures, measurements of the viscoelastic response in the medium−low frequency range are often beyond the sensitivity of the instrumental apparatus. Thus, the values of η''_{max} of these samples can be affected by errors stemming from extrapolation outside the measured frequency range.

The dynamic viscoelastic behavior of high polymers has often been described by the superposition of two retardation phenomena characterizing two distinct regions of the viscoelastic spectrum: the terminal region, at lower frequencies, and the transition region, at higher frequencies. For entangled networks of high molecular weight polymers, the transition zone takes the form of a plateau (the "rubbery plateau").[11] Separation between the two regions is well-pronounced for monodisperse polymers and, in general, for polymeric systems with long chains and narrow chain length distributions.[11] In contrast, a broad MWD results in extensive overlap of the two regions.

Several model calculations reported in the literature have successfully employed the following

expression to analyze the viscoelastic behavior of high polymers[12−14]:

$$J^*(\omega) = J_g + \frac{J_N^0 - J_g}{1 + (i\omega\tau_1)^{\beta_1}}$$

$$+ \frac{J_e^0 - J_g}{1 + (i\omega\tau_2)^{\beta_2}} + \frac{i}{\omega\eta_0} \quad (8)$$

where $J^*(\omega)$ is the complex compliance, J_g and $i/(\omega\eta_0)$ are the limiting values of $J^*(\omega)$ at high and low frequencies, and the two remaining terms describe $J^*(\omega)$ in the transition and in the terminal zone, respectively. Thus the transition zone is characterized by three parameters: the plateau compliance, J_N^0, a characteristic or principal relaxation time, τ_1, and β_1 which is a parameter related to the breadth of the retardation time spectrum in this region. The same meaning, referred to the terminal region is attached to the values of τ_2 and β_2, whereas J_e^0 is the equilibrium compliance.

The viscoelastic behavior of polymers of narrow MWD is satisfactorily described by this model.[14] However, it has been suggested that eq. (8) or its modifications can be of more general application[15,16] and the above-reported treatment has also been extended to some commercial homopolymer.[12] Thus, an attempt is made to apply eq. (8) to the copolymers investigated in this work. However, inspection of the G' and G'' curves reported in Figure 3 shows that only the terminal region of these curves, with just the very initial portion of the rubbery plateau, is experimentally accessible in the investigated ω-interval. Thus eq. (8) has been rewritten as

$$J^*(\omega) = J_g + \frac{J_e^0 - J_g}{1 + (i\omega\tau_2)^{\beta_2}} + \frac{i}{\omega\eta_0} \quad (9)$$

Nonlinear least-squares fitting of eq. (9) to the experimental $J^*(\omega)$ versus ω master curves, at $T_{ref} = 135°C$, confirmed that the viscoelastic behavior of the copolymers investigated in this work can be satisfactorily described by a retardation phenomenon in the terminal zone. This conclusion is also confirmed by the data reported in Figure 3, where experimental results are compared with the curves drawn on the basis of eq. (9). From these figures it also appears that most of the samples do not even reach the cross-over point in the $G'(\omega)$ and $G''(\omega)$ vs. ω curves. In fact this point

can be safely identified only in the 20PBABIP4 sample.

Table III reports values of J_e^0 and J_g obtained by the analysis of master curves at $T_{ref} = 135°C$. As regards J_e^0, it does not show significant changes in the investigated range of M_w and copolymer composition, a trend in agreement with that obtained by experiments and predicted by theories on the viscoelastic behavior of linear polymers.[4c,11] However, values of J_g in Table III display a correlation with M_w confirming that copolymer stiffness increases as molecular weight is increased.

A superposition of different curves of η^* versus ω can be obtained by using, for each test, its η_0-value as the shift factor. The result is a plot of the reduced viscosity, $\eta_{red}^* = \eta^*/\eta_0$, versus $\omega\eta_0$. This kind of plots provides a powerful tool to describe and analyze specific features of the viscoelastic behavior of polymer samples.[11,17,18] For polymers of narrow MWD, values of the reduced viscosity fall on the same curve, which is independent of temperature.[11] Such a plot is quite sensitive to effects stemming from polydispersity and chain branching that can be easily detected by changes in the slope of the reduced viscosity curves.[11] However, the use of η_0 as shift factor to build generalized master curves has been successfully extended also to polymers of broad MWD and high average molecular mass.[11,18] Figure 5 reports the master curve of reduced viscosities obtained for the samples investigated in this work. An attempt was made to fit experimental data by the following empirical expression[15,16]:

$$\eta_{red}^*(\omega) = \frac{1}{[1 + (i\omega\eta_0\tau_0)^{1-h}]^\beta} \qquad (10)$$

Values of the adjustable parameters in eq. (10) obtained by nonlinear least squares optimization are: $\tau_0 = 3.5 \times 10^{-6}$, $h = 0.29$ and $\beta = 1.3$. The solid line in Fig. 5 corresponds to the results of the fitting procedure. Some spreading of the experimental data can be detected, but agreement between observed and calculated values of the reduced viscosities is accurate within a standard deviation, σ, of 0.03. Thus, eq. (10) seems able to provide reliable estimates of the viscosities of these copolymer systems.

CONCLUSIONS

Industrial applications which make use of random copolymers can often take advantage of the spe-
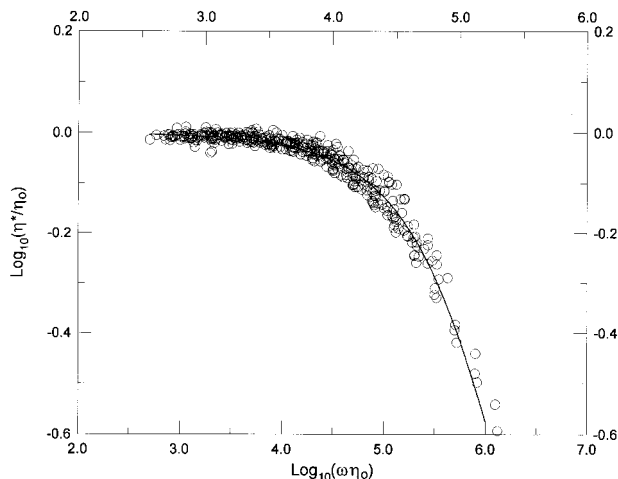
Figure 5 Generalized master curve for PBABIP copolymers. The solid line has been drawn according to results of the best fit to eq. (10).

cific character of these systems. In fact changes in the copolymer composition can lead to changes in the physical and chemical properties, which, in favorable cases, may encompass the whole range between the limits given by the two constituent homopolymers. On this ground, random PBABIP copolyesters can provide an interesting system, since the two corresponding pure homopolymers are used in several industrial processes. Thus, in the present work, attention has been focused on the correlations between the viscoelastic properties and the molecular parameters, like molecular weight and copolymer composition. Results obtained from dynamic shear testing and thermal characterization show that changes in the PBIP unit content have significant effects on the viscoelasticity and the thermal properties of the copolymers. Inspection of data in Table III shows that η_0 at $T_{ref} = 135°C$ increases as the isophthalate fraction is increased. For comparable values of M_w, this monotonic trend is valid for the investigated range of copolymer compositions, including the pure PBIP. An exception is given by the 20PBABIP4 sample which displays a much higher value of η_0. For the whole set of copolymer compositions, the dependence of the zero-shear viscosity on the molecular weight can be expressed as $\eta_0 = K M_w^a$. However, the values of a increase well above the "universal" value of 3.4 as the isophthalate content is increased. Such high values are attributable to the effect of a relatively large content of cyclic oligomers in the PBIP fractions, leading to significant decreases of the viscosities of the low-molecular weight samples.

More regular trends are obtained for the activation energy for viscous flow and G_0, a parameter related to the elastic behavior in the terminal zone. Both these parameters increase as the isophthalate fraction is increased. The relationships of E_a and G_0 with the structural characteristics of polymeric chains[4b,7] lead to the conclusion that by increasing the PBIP unit content the fractional free volume of these copolymers is reduced and the chain stiffness is increased. Changes in the values of T_g and T_m with copolymer composition reported in Table III are consistent with this conclusion.[2] At the molecular level, an increase in the PBIP unit content corresponds to substitutions of the $-(CH_2)_4-$ group with (see Scheme 1). It can be noted that the stiffening effect of these substitutions on the copolymer chain agrees with predictions based on the group contribution to the thermal and viscoelastic properties of polymers.[19]

The viscoelastic behavior of the copolyesters has also been analyzed in terms of the superposition of different retardation phenomena. In the investigated range of temperatures and frequencies, a viscoelastic model based on a single retardation phenomenon in the terminal zone seems able to provide a satisfactory description of the viscoelastic behavior of the copolymers. The computed limiting values of the complex compliances at high frequencies, J_g, display a correlation with M_w, leading to the conclusion that stiffer copolymers are obtained as molecular weight is increased. Dynamic testing of the PBABIP copolymers shows that the viscoelastic properties of these samples vary monotonically with composition and molecular weight, as expected for random copolymers. However, significant changes in the values of such functions are obtained in the whole range of copolymer composition. Thus, polymeric systems with different viscoelastic properties can be directly tailored by changing the comonomer ratio.

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