Thermal Characterization of Butadiene–Isoprene Copolymers with a 1,2/3,4 Structure

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ABSTRACT: Two series of butadiene–isoprene copolymers with a 1,2 and/or 3,4 structure were prepared at different polymerization temperatures, using $CrCl_2(dmpe)_2$-MAO as a catalyst system. Copolymerization carried out at higher temperature resulted in polymers in the whole range of monomeric ratio, from the highly crystalline 1,2-syndiotactic polybutadiene to the amorphous 3,4-polyisoprene. The molar composition of the butadiene–isoprene copolymers and the syndiotactic index of the butadiene sequences, represented as molar fraction of the syndiotactic pentads, were evaluated by carbon-13 nuclear magnetic resonance spectroscopy. The thermal behavior of the copolymers was investigated by differential scanning calorimetry. Nonisothermal crystallization kinetics were characterized by Ziabicki and Avrami methods as modified by Jeziorny. The crystallization and melting temperatures and the enthalpy of fusion of the copolymers were in good correlation with the syndiotactic index of butadiene sequences. The index was influenced by polymerization temperature and composition of butadiene–isoprene copolymers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2737–2743, 2003

Key words: differential scanning calorimetry (DSC); polybutadiene; syndiotactic; crystallization; melting point

INTRODUCTION

Several reports on the polymerization of butadiene to 1,2-polymer have been published[1–5] and many studies have been carried out on the thermal properties of this polymer.[6–10] In particular, highly crystalline 1,2-syndiotactic polybutadiene, with a melting point of ~210°C, has been obtained with cobalt catalysts.[2–4] However, to permit better processability, 1,2-polybutadiene with lower melting point and moderate crystallinity is of practical interest for use as an elastomer in combination with other products.

Catalysts that are capable of making 1,2-polybutadiene with such characteristics are reported in some patents and consist of a cobalt compound, an aluminum–alkyl, and a modifier. Depending on the nature of the modifier, a 1,2-polybutadiene with a different melting point can be obtained.[11–16]

Recently, we have reported on the polymerization of 1,3-dienes with $CrCl_2(dmpe)_2$-MAO.[17] This system is also able to copolymerize butadiene and isoprene, giving copolymers with a 1,2/3,4 structure.[18] These copolymers are semicrystalline or amorphous, depending on the isoprene content, and the melting point can be accurately controlled by varying the isoprene content in the feed.

In this paper, we report the results of a detailed investigation, using differential scanning calorimetry (DSC), of the crystallization and thermal behavior of butadiene–isoprene copolymers. The influence of the copolymer composition and of the syndiotactic index on the thermal properties was determined for the samples prepared at two different temperatures using the catalyst system $CrCl_2(dmpe)_2$-MAO. The nonisothermal crystallization kinetics of both copolymer series were also analyzed by various theoretical approaches.

EXPERIMENTAL

Synthesis

The preparation of the reagents employed in this work has been extensively reported in a previous paper.[18] The polymerizations were carried out under nitrogen in a 50-mL glass reactor. Isoprene and toluene were introduced in the reactor containing butadiene kept at −20°C, and the solution so obtained was brought to the desired polymerization temperature. Methylaluminoxane (MAO) and $CrCl_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] were then added as toluene solutions.[18] Polymerizations were stopped by adding methanol containing hydrochloric acid. After washing with methanol, the polymers obtained were dried at room temperature *in vacuo*.

Two series of butadiene–isoprene copolymers were prepared at −30 and 20°C, respectively. The copoly-

merization carried out at 20°C resulted in samples covering the whole monomeric ratio, ranging from highly crystalline 1,2-syndiotactic polybutadiene to completely amorphous 3,4-polyisoprene. At −30°C, copolymers with a high content of butadiene were obtained.

Polymer characterization

Intrinsic viscosity was determined in o-dichloroben-zene at 135°C or in toluene at 25°C with a Desreux–Bischof viscometer.

Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra were acquired on a Bruker AM 270 instrument. Polymer samples were dissolved in $C_2D_2Cl_4$ at 103°C using hexamethyldisiloxane as internal standard. The concentration of the polymer solutions was ~10 wt %.

The molar compositions of butadiene–isoprene copolymers , X_B and X_I, respectively, were evaluated from ^{13}C NMR by the following relationships:

$$X_B = A_B/(A_B + A_I) \text{ and } X_I = 1 - X_B \qquad (1)$$

where A_B is the total sum of the integrated areas of the resonances around 112 ppm, due to the olefinic methylene carbon of the butadiene unit, and A_I is the total sum of the integrated areas of the resonances around 110 ppm, due to the olefinic methylene carbon of the isoprene unit. The syndiotactic index of the butadiene sequences, represented as molar fraction of the syndiotactic pentads [rrrr], was evaluated from the integrated areas of the peaks around 112 ppm, corresponding to the different butadiene pentads, as reported in the literature.[10,19,20]

Thermal analysis

DSC scans were carried out on a Perkin-Elmer Pyris 1 instrument equipped with a liquid subambient device. Typically, ~5 mg of polymer were weighed into an aluminum pan and heated from −150°C to ~20°C above the fusion temperature under a helium atmosphere (30 mL/min) at a scan rate of 20°C/min and then cooled to 0°C at a cooling rate of 20°C/min.

The melting temperature (T_m), the enthalpy of fusion (ΔH_m), and the crystallization temperature (T_c) were recorded for the semicrystalline samples. The exothermal curves of heat flux as a function of temperature were characterized by nonisothermal melt crystallization kinetic investigation. The glass transition temperature (T_g) was calculated for amorphous polymers at the temperature corresponding to the midpoint of the transition.

TABLE I
Composition, Syndiotactic Index, and Glass Transition Temperature of Polyisoprene and Butadiene–Isoprene Copolymers

Sample	X_I	[rrrr]	T_g (°C)
H14	0.165	0.462	7
H15	0.184	0.424	6
H16	0.192	0.42	6
H17	0.262	0.37	4
H18	0.315	0.334	3
H19	0.328	0.408	3
H20	0.384	0.255	2
H21	0.415	0.202	2
H22	1.00	—	29

RESULTS AND DISCUSSION

The molar composition and microstructure of butadiene–isoprene copolymer series, determined by ^{13}C NMR, are reported in Tables I and II.The thermal behavior of the copolymers is strongly influenced by composition. Typical thermograms of copolymers with different monomeric ratios, synthesized at 20°C, are shown in Figure 1.The copolymers containing >16 mol % isoprene showed a T_g of 2–7°C , as reported in Table I. The samples containing >20 mol % isoprene were completely amorphous, although a low degree of crystallinity was observed for H14, H15, and H16 samples (Table II).

The other semicrystalline samples (H1–H13 and L-series) were quenched from the melt in liquid nitrogen. The adopted quenching procedure was unable to produce amorphous samples, and the absence of thermal events was registered by DSC from −150°C to the melting peak for pure polybutadienes and copolymers.

All samples shown in Table I present a value of intrinsic viscosity calculated in toluene at 25°C of ~2 dL/g corresponding to a molecular weight >100,000; therefore, the aforementioned T_g values can be considered constant and independent of molecular mass. The T_g of 3,4-polyisoprene prepared with the same catalyst system at 20°C is also given in Table I.

The dependence of the T_g on random copolymer composition has been essentially explained by Gordon–Taylor, and Di Marzio–Gibbs equations.[21,22] These approaches fail when the T_g versus composition curve exhibits a minimum with values below the T_gs of the respective homopolymers. This behavior has been reported in the literature for various random copolymers.[23,24]

The T_g of butadiene–isoprene copolymers was lower than the experimental T_g of 3,4-polyisoprene (Table I), and lower than the T_g value reported in literature for syndiotactic 1,2-polybutadiene.[2]

The experimental T_g values versus composition curve, reported in Figure 2, can be well fitted by the following semiempirical equation:

TABLE II
Composition, Syndiotactic Index, and Thermal Properties of Polybutadienes and Semicrystalline Butadiene–isoprene Copolymers

Sample	X_B	[rrrr]	T_m (°C)	ΔH_m (J/g)	T_c (°C)
$T_{polymerization} = -30°C$					
L1	1.00	0.90	198	78.3	169
L2	0.985	0.86	194	70.9	166
L3	0.980	0.785	189	72.0	158
L4	0.978	0.85	185	74.3	151
L5	0.948	0.792	177	67.6	140
L6	0.927	0.704	163	49.5	126
$T_{polymerization} = 20°C$					
H1	1.00	0.749	162	54.9	124
H2	0.985	0.662	152	47.3	118
H3	0.977	0.67	150	43.7	117
H4	0.974	0.672	148	41.8	103
H5	0.971	0.655	142	39.5	108
H6	0.968	0.614	132	30.1	97
H7	0.961	0.622	141	36.1	101
H8	0.954	0.62	128	29.7	96
H9	0.935	0.575	123	28.1	89
H10	0.918	0.55	119	24.9	85
H11	0.900	0.557	107	15.5	70
H12	0.889	0.541	100	12.0	63
H13	0.853	0.506	89	8.2	53
H14	0.835	0.462	49	2.9	37
H15	0.816	0.424	54	2.4	37
H16	0.808	0.42	52	1.6	—

$$T_g = B'\omega_1\omega_2 + T_{g1}\,\omega_1 + T_{g2}\,\omega_2 \qquad (2)$$

where $T_{g,i}$ and ω_i are the T_gs and the weight fractions of the components, respectively. The best fitting of eq. 2 to the experimental T_g was found when the B' parameter was equal to -84, and a T_g of 18°C was extrapolated for pure 1,2-syndiotactic polybutadiene.

Copolymers with a butadiene content >80 mol % appear as semicrystalline materials. The thermal properties of crystalline copolymers obtained at -30 and 20°C are reported in Table II. The copolymers prepared at $-30°C$ present T_m values higher than those synthesized at 20°C, at constant composition. In fact, the slower kinetic of polymerization observed at $-30°C$ allowed a higher stereoregularity to be obtained in the synthesis of butadiene sequences.[17]
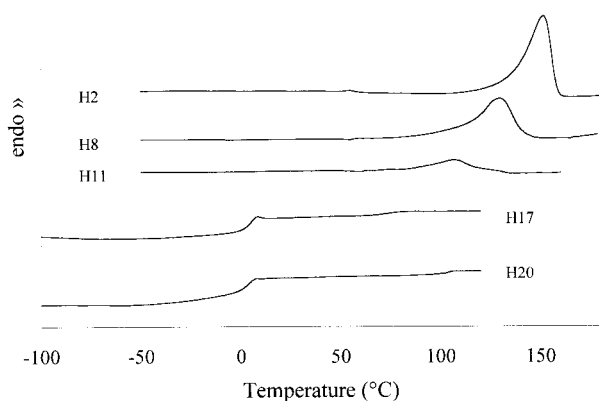
The melting points collected in Table II are plotted as a function of the logarithm of the butadiene molar fraction in Figure 3. Two different trends corresponding to the copolymer groups synthesized at the temperatures of -30 and 20°C were observed. A unique straight line, independent of the copolymerization temperatures, was observed in the plot of the T_m values versus the logarithm of the molar fraction of syndiotactic butadiene pentads (Figure 4). This result indicates a biunivocal correlation between T_m and the syndiotactic index. The T_m of the random copolymer would be mainly due to the syndiotactic pentads, [rrrr], of the crystallizable comonomer.

By plotting T_m versus $-\ln[rrrr]$, a melting point of 225°C was extrapolated for the totally syndiotactic

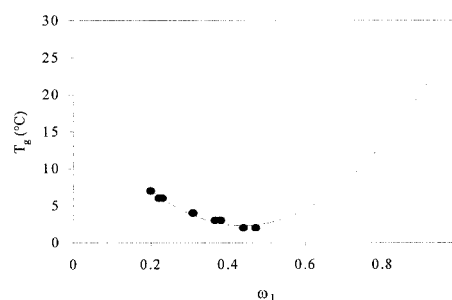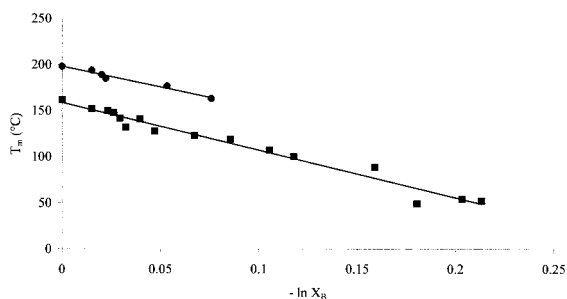**Figure 1** DSC heating scans (20°C/min) of some butadiene–isoprene copolymers prepared at 20°C.

Figure 2 Plot of T_g versus ω_1 for butadiene–isoprene copolymers of Table I.
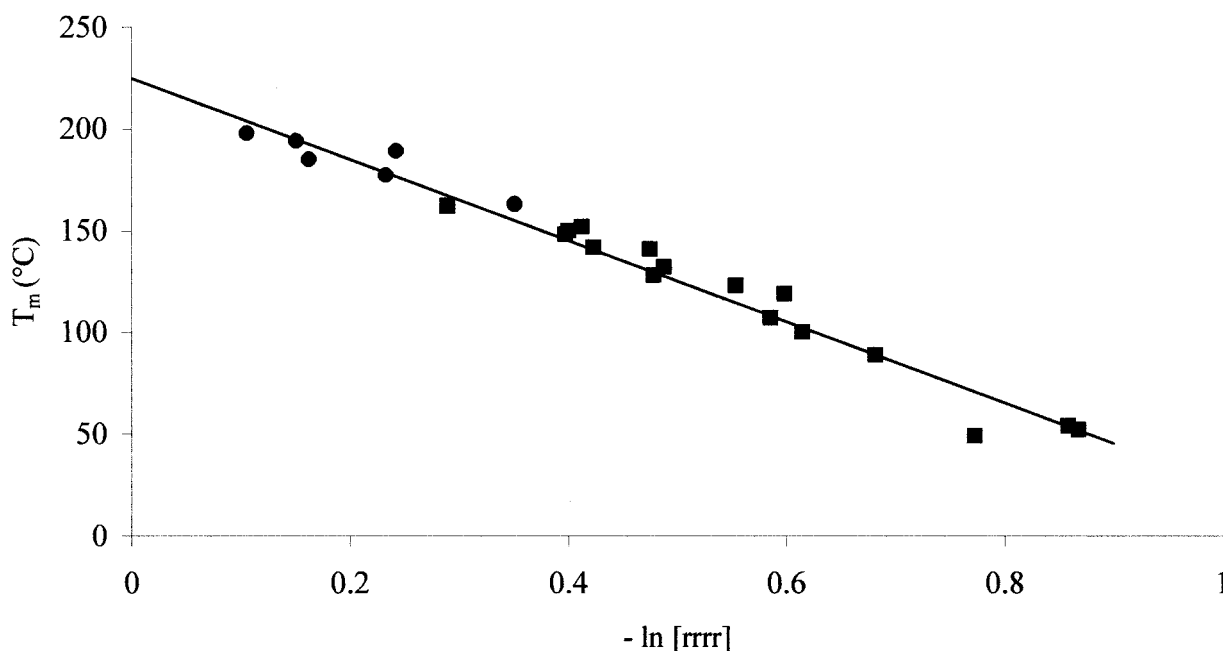
Figure 3 Plot of T_m versus $-\ln X_B$ for butadiene–isoprene copolymers of Table II. Key: (●) $T_{polymerization} = -30°C$; (■) $T_{polymerization} = 20°C$.

homopolymer 1,2-polybutadiene, characterized by [rrrr] = 1. This value is comparable to the one obtained for the syndiotactic homopolymer 1,2-polybutadiene prepared by a cobalt-based catalyst system.[2–4,10]
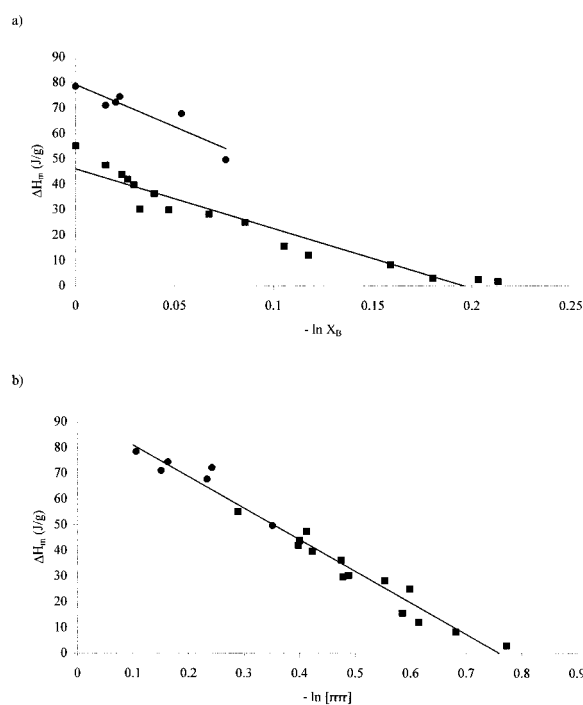
As can be seen in Table II, the ΔH_m values decrease progressively on going from 78 J/g for the homopolymer L1 to 2 J/g for the copolymer containing ~20 mol % isoprene units. These data confirm the strong influence of isoprene content on the crystallinity of the polymer material.

Analogous to the trend observed for the melting points, a good correlation between the ΔH_m values and the syndiotactic index of the copolymers was found (Figure 5).

As shown in Figure 5a, two distinct trends were found by plotting the heat of fusion versus the molar fraction of butadiene. A single straight line fits well all
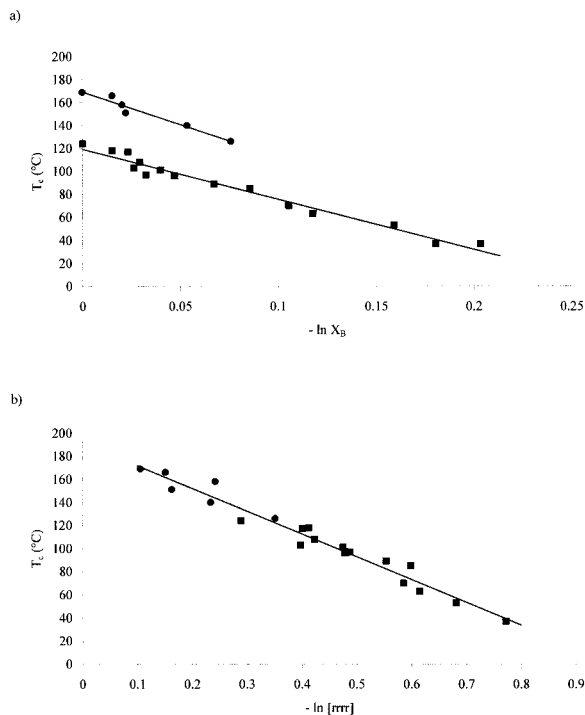

Figure 5 Relationship of ΔH_m versus (a) $-\ln X_B$ and (b) $-\ln$ [rrrr] for butadiene–isoprene copolymers of Table II. Key: (●) $T_{polymerization} = -30°C$; (■) $T_{polymerization} = 20°C$.

the experimental ΔH_m values as a function of [rrrr] (Figure 5b).

A valuable correlation with the syndiotactic index has been also observed for T_c values, obtained by cooling the butadiene–isoprene copolymers from the melt at 20°C/min (Figure 6).

Figure 4 Plot of T_m versus $-\ln$ [rrrr] for butadiene–isoprene copolymers of Table II. Key: (●) $T_{polymerization} = -30°C$; (■) $T_{polymerization} = 20°C$.

a)

b)

Figure 6 Plot of T_c versus (a) $-\ln X_B$ and (b) $-\ln$ [rrrr] for butadiene–isoprene copolymers of Table II. Key: (●) $T_{\text{polymerization}} = -30°C$; (■) $T_{\text{polymerization}} = 20°C$.

The L-series copolymers and eight selected samples of the H-series, with a heat of crystallization >10 J/g, were characterized by a nonisothermal crystallization investigation. The crystallization exotherms for different butadiene–isoprene copolymers are reported in Figure 7.The results show that for nonisothermal melt crystallization conducted at a constant cooling rate, the T_c shifts to a lower temperature region as the isoprene fraction increased.

As suggested by Jeziorny, the kinetics of nonisothermal crystallization can be characterized by the application of two different procedures.[25] One procedure is based directly on the approximate theory, formulated by Ziabicki, in which the crystallization can be represented by the equation for first-order kinetics:[26–28]

$$dX_t/dt = [1 - X_t]K(T) \quad (3)$$

where the rate constant, $K(T)$, is dependent only on temperature, and X_t is the weight fraction of the material crystallized at time t. The value of X_t is calculated by

$$X_t = \int_0^t (dH/dt)dt \Big/ \int_0^\infty (dH/dt)dt \quad (4)$$

where the first integral is the heat generated at time t and the second is the total heat when the crystallization is complete. A value for $K(T)$ can be determined at a temperature T in the range of temperatures between glass transition and melting temperatures.

The quantity G, defined as "the kinetic crystallizability" can be calculated by:

$$G = \int_{T_g}^{T_m} K(T)dT = (\pi/\ln2)^{1/2} K_{\text{max}} D/2 \quad (5)$$

where K_{max} is the value of $K(T)$ at the maximum crystallization rate, and D is the half-width of the crystallization peak. The parameter G must be corrected considering the effect of cooling rate (dT/dt), and its final form is as follows:
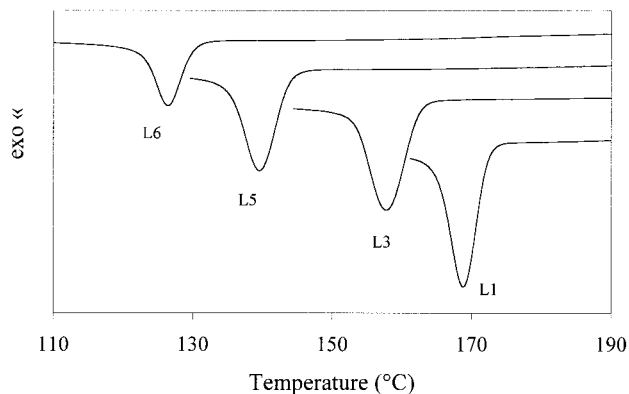
$$G_c = G/(dT/dt) \quad (6)$$

where G_c means the kinetic crystallizability at unit cooling rate.

Calculation of the G_c parameter was made possible by knowing the D and K_{max} values in eq. 5. The half-width D can be directly determined from the thermogram, and the K_{max} value can be calculated as follows:

$$K_{\text{max}} = C_k/t_{\text{max}} \quad (7)$$

where:

$$C_k = \int_0^{t_{\text{max}}} (dH/dt)dt \Big/ \int_{t_{\text{max}}}^\infty (dH/dt)dt \quad (8)$$

Figure 7 DSC crystallization curves of some butadiene–isoprene copolymers cooling from molten state at 20°C/min.

where t_{max} is the time from the start of crystallization to the time at which the maximum rate of crystallization is reached. The G_c values reported in Table III show a quite constant value for all investigated copolymers.

The second procedure is based on the acceptance of the simplifying assumption that crystallization occurs under constant temperature. In this case, the method to describe the crystallization kinetic is based on the Avrami equation, which assumes that the relative degree of crystallinity developed within crystallization time:

$$1 - X_t = \exp\left(-Z_t t^n\right) \qquad (9)$$

where n is a parameter depending on the type of nucleation and on the geometry of the growing crystals, and Z_t is the overall kinetic constant involving both nucleation and growth rate parameters.

Considering the nonisothermal character of the process investigated, the Z_t value determined must be corrected for the effect of cooling rate:

$$Z_c = Z_t/(dT/dt) \qquad (10)$$

The values of n and Z_t were derived from the slope and the intercept, respectively, of the straight lines obtained by plotting $\log[-\ln(1 - X_t)]$ versus $\log t$.

The Avrami plot for the L-series and for the H-series copolymers, with an X_B value >0.918, presented two linear trends with different slopes. Deviation from the initial linear trend, observed for these copolymers when the X_t value was ~0.8, was considered due to secondary crystallization phenomena. The copolymers with higher isoprene content showed a single linear trend (Figure 8).

The Avrami exponents reported in Table III were calculated from the initial slope. The n values observed for the H-series copolymers were low and dispersed around

TABLE III
Nonisothermal Crystallization Kinetics of Polybutadienes and Butadiene–Isoprene Copolymers Determined by Ziabicki and Avrami Method

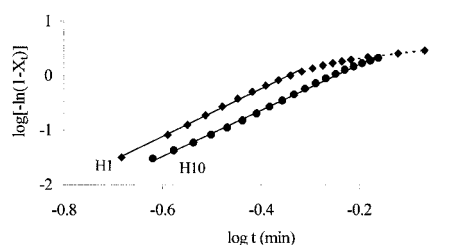| Sample	T_c (°C)	G_c	n	Z_c (min^{-n}/°C)
L1	169	1.31	4.4	1.22
L2	166	1.12	4.5	1.16
L3	158	1.25	3.8	1.16
L4	151	1.47	4.3	1.19
L5	140	1.16	4.5	1.15
L6	126	1.21	4.7	1.17
H1	124	1.09	4.1	1.17
H2	118	1.30	4.0	1.10
H4	103	1.35	4.1	1.08
H8	96	1.48	4.0	1.09
H9	89	1.38	3.9	1.08
H10	85	1.23	4.0	1.08
H11	70	1.24	4.0	1.06
H12	63	1.20	3.9	1.13

Figure 8 Plot of $\log[-\ln(1 - X_t)]$ versus $\log t$ for nonisothermal melt crystallization of H1 and H10 copolymers.

the integral value of 4. The L-series copolymers generally showed more dispersed values, from 3.8 to 4.7. However, the results relative to the primary crystallization suggest that the nucleation mechanism and crystal growth geometries were similar for both series of all investigated composition. The value of the Avrami exponent equal to 4 correspond to a three-dimensional spherical growth with thermal nucleation.[30]

As observed for the G_c values, the calculated Z_c values reported in Table III show quite a constant value for both series of copolymers that is independent from the monomeric ratio.

CONCLUSIONS

Two series of butadiene–isoprene copolymers with a 1,2/3,4 structure were prepared at −30 and 20°C using the catalyst system $CrCl_2(dmpe)_2$-MAO. The copolymerization carried out at the lower temperature resulted in copolymers with a higher syndiotactic index of the butadiene sequences, at constant molar composition. The syndiotactic index decreased with the increasing of the isoprene fraction for both series of copolymers.

The thermal behavior of butadiene–isoprene copolymers was strongly influenced by composition and polymerization conditions. The glass transition phenomenon was observed for the samples containing >20 mol % isoprene units. Copolymers with a butadiene content >80 mol % were semicrystalline, and their melting temperature decreased with increased amounts of isoprene.

The crystallization and melting temperatures and the enthalpy of fusion of the copolymers were in good correlation with the syndiotactic index of butadiene sequences.

The parameters of nonisothermal crystallization kinetics indicated that the kinetic crystallizability and nucleation mechanism of both series of copolymers were independent of composition.

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