Crystallization Kinetics of *cis*-1,4-Polybutadiene

Maria Laura Di Lorenzo

Istituto di Chimica e Tecnologia dei Polimeri, c/o Comprensorio Olivetti, Via Campi Flegrei 34, 80078 Pozzuoli (NA), Italy

ABSTRACT: The isothermal and nonisothermal crystallization kinetics of *cis*-1,4-polybutadiene has been investigated with respect to the content of *cis* units and the linearity of the main chain. The rate of spherulite growth increases with chain regularity as the presence of branches as well as segments with different configurations slows the crystallization rate. The major parameter that determines the crystallization rate is the presence in the formulation of heterogeneities that favor the formation of primary nuclei and determine an anticipated onset of crystallization. As the activity of the heterogeneous nuclei depends more on the type and number of foreign particle than on any chain parameter, no straightforward information on the influence of the chain structure on the crystallization rate can be derived by mere calorimetric analysis, at least for analyzed samples. It is only with combined analysis by optical microscopy that comprehensive information on the crystallization kinetics of *cis*-1,4-polybutadiene can be derived. The results reported in this contribution point out the importance, in polymer science, of preferring complementary instrumentation and not limiting experimental investigations to a single technique of analysis. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1408–1413, 2010

Key words: crystallization; nucleation; polybutadiene

INTRODUCTION

Polybutadiene (PBD) with a large number of *cis*-1,4 units is one of the most common materials produced by the synthetic rubber industry. This polymer is widely used for the production of tires, a market segment that covers about 70% of the world's PBD production.[1] A number of different technologies with Ziegler–Natta catalysts can be used in the commercial production of PBD with high *cis*-1,4 repeating unit levels: titanium, uranium, cobalt, nickel, and neodymium are the mostly commonly used metals in these catalyst systems.[2,3]

Many grades of *cis*-1,4-polybutadienes (*cis*-PBDs) have been developed. Structural variables include the molecular weight and its distribution, the stereospecificity, and the branching content. Depending on the microstructure, different properties and processabilities can be achieved. The cobalt systems produce a highly branched PBD with a low solution viscosity that is used as a polystyrene and acrylonitrilo-butadiene-styrene copolymer (ABS) modifier. The nickel catalysts make PBD with an intermediate level of branching. Low *cis*-PBD can be obtained with the alkyl lithium catalyst system, which yields a polymer with about 40% *cis*, 50% *trans*, and 10% vinyl units.[4] The neodymium-based catalysts are the most commonly used today because of their environmental safety. These systems allow the production of a highly stereospecific and linear polymer without branches that has the best tensile and hysteresis (low heat buildup) properties of all the high-*cis* types, as none of the catalytic systems previously identified (e.g., nickel- or cobalt-based ones) for the *cis*-1,4 polymerization of butadiene show these characteristics.[5,6]

However, a strictly linear structure of PBD results in high cold flowability. This drawback can be avoided by the incorporation of a certain number of branches into the polymer chain.[5] The introduction of branches into a linear structure leads to a series of additional applicative advantages and above all to an improvement of processability. However, the presence of branching is expected to induce considerable changes in the crystallization behavior of a linear polymer, which needs to be quantified for a proper assessment of the structure–processing–property triangle. The rate under which a polymer solidifies from the melt determines the morphology and thus the properties of the final products. This underlines the interest in the investigation of the effects of molecular parameters such as chain linearity and regularity on the crystallization kinetics of *cis*-PBD.

Few data have appeared in the literature on the influence of the molecular mass and other structural parameters on the crystallization kinetics of *cis*-PBD, and they are related only to the isothermal crystallization of polymers produced by uranium-, nickel-, titanium-, and cobalt-based catalysis[7–9] or to the

TABLE I
Molecular Characteristics of the *cis*-PBD Grades

Code	*cis* (%)	M_w (kDa)	M_n (kDa)	M_w/M_n	Structure
98-li	98	437	148	2.95	Linear
98-sb	98.4	427	138	3.1	Slightly branched
97-li	97	377	152	2.48	Linear
97-sb	97	380	100	3.8	Slightly branched
95-al	95	326	136	2.4	Almost linear

strain-induced crystallization of as-polymerized[10,11] and crosslinked *cis*-PBD.[12,13] The studies conducted on the quiescent crystallization of noncrosslinked *cis*-PBD prepared by a cobalt-based catalyst detail the effects of the molecular mass and branching on the growth rate and morphology of *cis*-PBD spherulites.[8,9] The influence of the type of catalyst on the isothermal bulk crystallization of *cis*-PBD is described in ref. 7 for polymers prepared with uranium-, nickel-, titanium-, or cobalt-based systems. However, to our knowledge, no thorough investigation of the crystallization of *cis*-PBD produced with modern and environmental friendly catalysts based on neodymium compounds has appeared in the literature.

In this contribution, a thorough investigation of the crystallization kinetics of *cis*-PBD, conducted by isothermal and nonisothermal methods, is presented. The study refers to polymers with different *cis* contents as well as different levels of branching that are produced with modern catalytic systems based on rare-earth compounds. Detailed knowledge of the crystallization and melting behavior of PBD is expected to enable the optimization of its thermal properties through the control of its crystallinity and supermolecular structure.

EXPERIMENTAL

Materials

cis-PBD samples with different microstructures were specifically synthesized for this study with neodymium-based catalytic systems. They were kindly provided by Polimeri Europa S.p.A. (Ravenna, Italy). The molecular characteristics of the analyzed grades are given in Table I, which reports the weight-average molecular mass (M_w) and number-average molecular mass (M_n), the molecular mass distributions, and information on the linearity and degree of branching of the used materials. The various samples were identified by a notation code, shown in the first column of Table I, that is based on the contents of *cis* units and branching.

Calorimetry

Thermal properties were measured with a Mettler DSC822[e] (Mettler-Toledo, Inc., Columbus, OH) equipped with a liquid-nitrogen cooling system. The instrument was calibrated with respect to temperature with high-purity standards (indium, naphthalene, and cyclohexane) and with respect to energy with the heat of fusion of indium. Dry nitrogen was used as a purge gas at a rate of 50 mL/min. Each measurement was repeated three times to improve accuracy.

To investigate the overall kinetics of isothermal crystallization, PBD samples were heated from room temperature to 70°C at a rate of 20°C/min, equilibrated at 70°C for 3 min, and then cooled at 30°C/min to the desired isothermal crystallization temperature (T_c), at which they were allowed to crystallize. The T_c values ranged from −30 to −18°C. Lower temperatures were not investigated as crystallization could start during cooling to T_c. At higher temperatures, crystallization is rather slow, and this leads to a poor signal-to-noise ratio and a high experimental uncertainty.

Nonisothermal crystallization analyses were conducted at various cooling rates ranging from 1 to 10°C/min after heating of the material from room temperature to 70°C at 20°C/min followed by 3 min of isotherm at 70°C. Cooling rates higher than 10°C/min were not investigated to limit the problems due to thermal gradients within the sample and between the cooling furnace and the sample, which could result in an inexact monitoring of the sample temperature during the phase transition.[14]

Optical microscopy

Spherulite growth rates were estimated by optical microscopy with a Zeiss (Carl Zeiss, Inc., Thornwood, NY) polarizing microscope equipped with a Linkam TMHS 600 (Linkam Scientific Instruments, Ltd, Tadworth, Surrey, UK) hot stage and a Linkam CS 196 unit for fast cooling with liquid nitrogen. Samples for optical microscopy analysis were prepared via the casting of a drop of a 2% toluene solution onto a glass slide followed by drying *in vacuo*. The radius of the growing crystals was monitored during solidification by photomicrographs taken at appropriate intervals of time with a JVC TK-1085E video camera. Spherulite radii were measured with Image-Pro Plus 3.0 software. Dry nitrogen gas was purged throughout the hot stage during all measurements and thermal treatments.

The thermal treatments before isothermal crystallization were identical to those used in calorimetry, and again, each measurement was repeated three times. Spherulite growth rate data were obtained under isothermal conditions from the initial slope of radius–time plots.[14]

RESULTS AND INITIAL DISCUSSION

The crystallization kinetics of cis-PBD was investigated with differential scanning calorimetry (DSC) under isothermal and nonisothermal conditions. For the isothermal analyses, a temperature range in which all the analyzed polymers crystallize in a reasonable time was selected to better compare the crystallization behaviors of the various grades. For the chosen temperature range, a cooling rate of 30°C/min from 70°C to the desired T_c was sufficient to prevent crystallization during cooling. However, for the faster crystallizing grades, it was found that at a few T_c's, crystallization started during the instrumental drift that took place after the preset isothermal point was reached. In a DSC apparatus, because of the finite response time of the cell temperature controller, a sharp change in the scanning rate (e.g., a switch from cooling to an isothermal step) always produces a transient overshoot, after which the signal gradually returns to the steady state.[15] If the initial stages of the phase transition are masked by this overshoot, the latter needs to be separated from the exotherm associated with crystallization to estimate the time dependence of the evolved latent heat and determine the kinetics of phase transformation. To do this, after isothermal crystallization, blank experiments were performed with the same sample at a temperature above the melting point, at which no transition took place.[16–18] The blank runs were subtracted from the crystallization exotherms, and the intersection of the extrapolated baseline with the resulting exothermal curve was taken as the starting time for the phase transition according to the procedure detailed in ref. 19. The heat that evolved during crystallization was recorded as a function of time, and the fraction of material that crystallized after time t (X_t) was calculated from the ratio of the heat generated at time t to the total heat that developed during the phase transformation. From a plot of X_t against time, the half-time of crystallization, defined as the time needed for 50% of the final crystallinity to develop, was obtained.

The half-times of crystallization of the analyzed cis-PBD samples are reported in Figure 1 as a function of temperature. As expected, in the analyzed range, the phase-transition rate decreases with the temperature of analysis. Figure 1 reveals that the
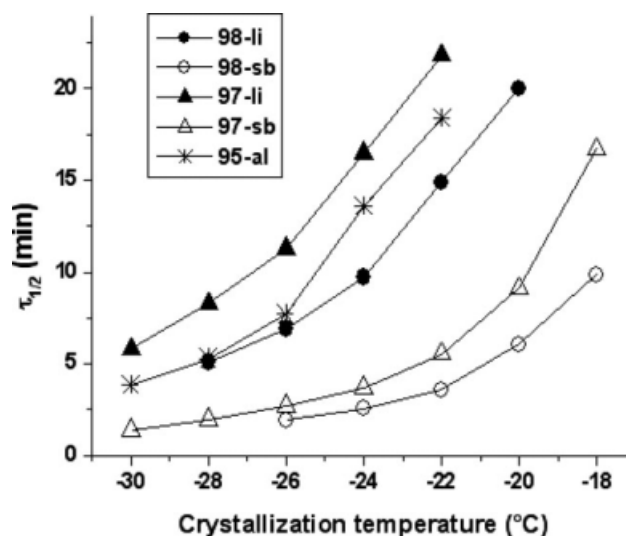

Figure 1 Half-time of crystallization ($\tau_{1/2}$) of cis-PBD as a function of T_c.

branched cis-PBD grades crystallize faster than the linear ones. The slowest transition rate is attained by the polymer with a linear chain that has 97% cis units (97-li), whereas the highest crystallization rates are typical of the two branched samples with high cis contents (98-sb and 97-sb).

The data shown in Figure 1 are rather unexpected as crystallization rates generally increase with chain linearity and stereoregularity. The introduction of a higher concentration of units of different configurations should lead to slower phase-transition kinetics. Similarly, the disentanglement of chains with long branches is difficult as the reptation time increases with the branch length.[20] Short branches also retard crystallization because they may act as defects trapped within the crystal structure or as noncrystallizable species that need to be expelled from the crystals.[21] The molecular mass also influences crystallization because the motion of the polymer chains toward the growing crystals is slowed for longer chains, but the range of variation of the molecular mass of the used cis-PBD grades, shown in Table I, should lead to only a minor influence on the crystallization rate.[22]

Additional information on the crystallization kinetics of cis-PBD comes from the analysis of the induction time needed to initiate isothermal crystallization. The data are presented in Figure 2. Similarly to the half-time of transition data, it is not easy to identify a specific trend of the induction time with the chain microstructure. Crystallization has a fast onset in the polymers with a branched structure without an apparent correlation with stereospecificity.

Nonisothermal crystallization analysis of cis-PBD is presented in Figures 3 and 4. Figure 3 illustrates heat-flow rate plots of the various PBD grades
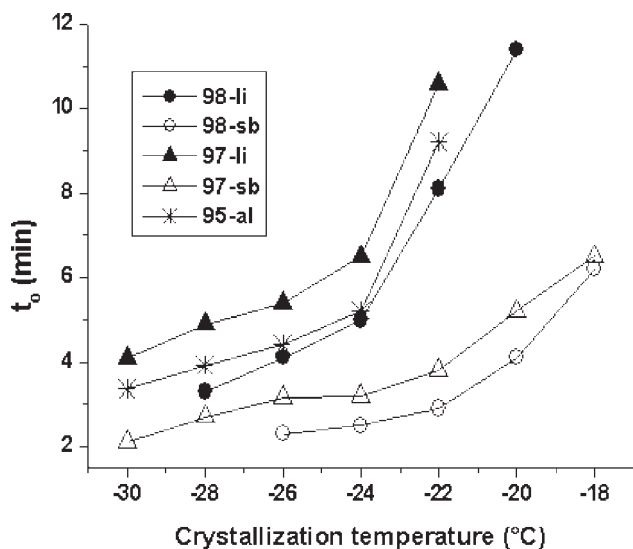
Figure 2 Onset time of crystallization (t_o) of cis-PBD as a function of T_c.

obtained during cooling from the melt at 10°C/min. In Figure 4(a,b), the onset and peak temperatures of the crystallization exotherms of the different samples are compared with respect to the cooling rate. The onset point was taken as the intersection point of the baseline before the transition and the inflectional tangent, and the peak temperature was taken as the maximum of the exotherm. As expected, an increase in the cooling rate results in a shift of the phase-transition parameters of all the analyzed polymers toward lower temperatures: at low cooling rates, there is more time to form the nuclei, so crystallization starts at higher temperatures.[23] Not predictable is instead the trend of the crystallization kinetics
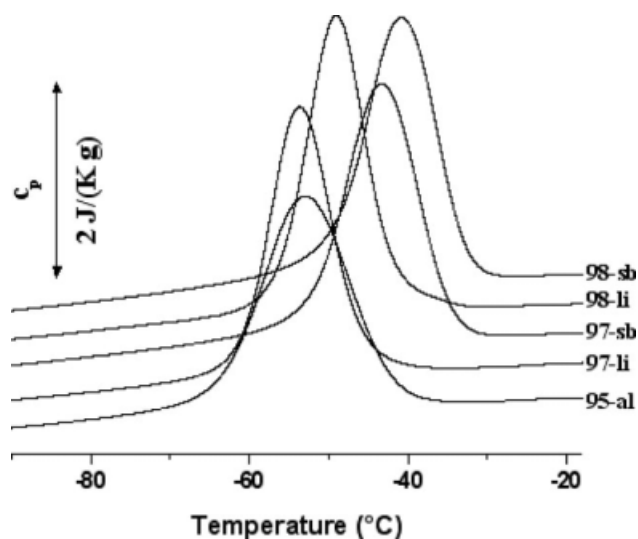

Figure 3 Experimental specific heat capacity (c_p) of cis-PBD during cooling from the melt at 10°C/min. The curves are shifted along the y axis for clarity of presentation.
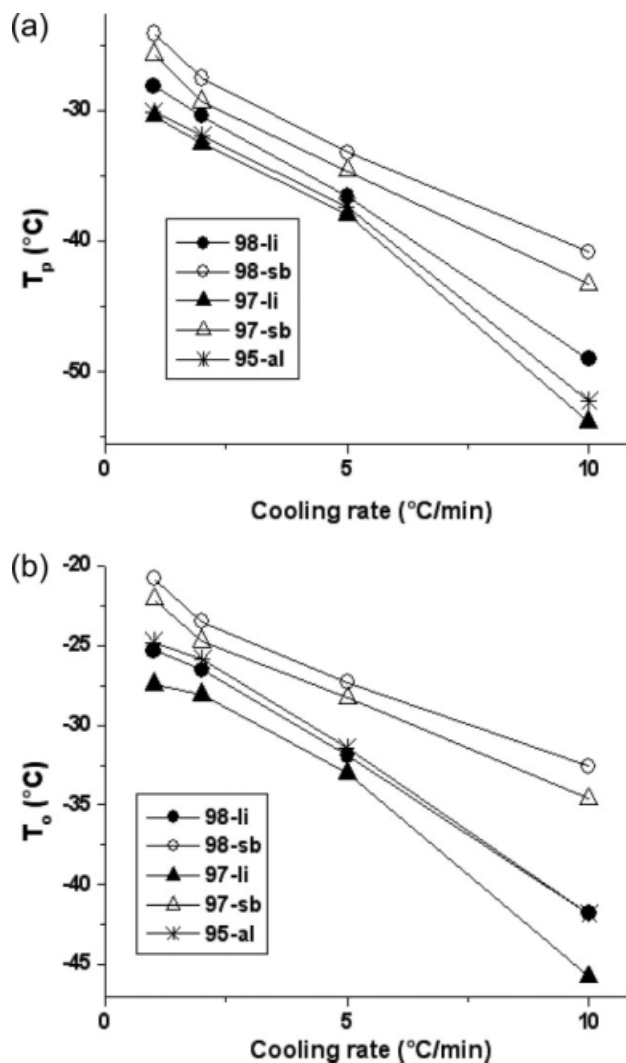

Figure 4 (a) Peak temperature (T_p) and (b) onset temperature (T_o) of crystallization of cis-PBD as a function of the cooling rate.

with the chain structure. As shown in both Figures 3 and 4, the linear cis-PBD grades have a retarded onset of the phase transition in comparison with the branched polymers, and no trend of the crystallization exotherm with the fraction of cis units in the chain can be identified. However, it is important to note that, despite the lack of correlation of the values shown in Figures 3 and 4 with the available data on the chain structures of the various grades used, the results of nonisothermal crystallization analysis parallel the information gained by the crystallization experiments performed under isothermal conditions (illustrated in Figs. 1 and 2), as the polymers that display fast or slow crystallization kinetics in nonisothermal analysis have the same relative trend under isothermal conditions.

The crystallization rate of cis-PBD was analyzed also by optical microscopy. Figure 5 reports the rate of radial growth of cis-PBD spherulites as a function
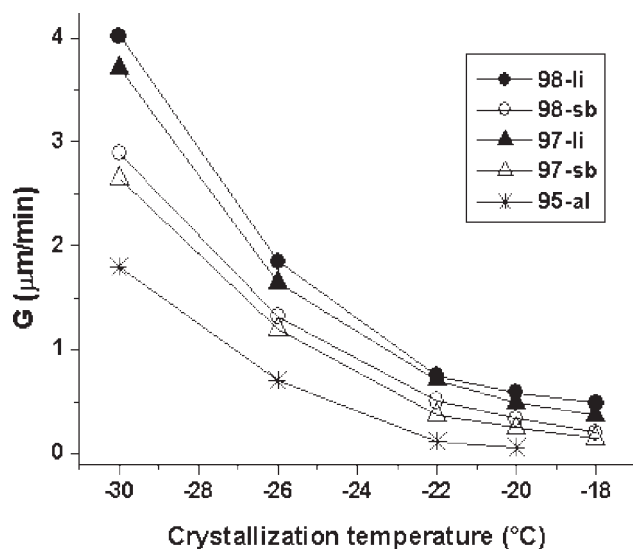
Figure 5 Spherulite radial growth rate (G) of *cis*-PBD as a function of T_c.

of the T_c values for the various analyzed polymers. Contrary to the DSC data shown previously, a clear picture appears from optical microscopy analysis. The rate of crystal growth increases with chain regularity as faster transition rates are observed for the polymers that have linear chains. For the same fraction of *cis* units, the advance of the crystal growth front is faster in the *cis*-PBD grades with a linear structure. For the analyzed compositions, the influence of the *cis* content is also of importance, but somewhat less pronounced than the linearity of the main chain. This may be ascribed to the low range of variation of the *cis* fraction in the analyzed materials because the influence of stereospecificity on the crystal growth rate becomes significant when 5% of the repeating units with a *cis* configuration are replaced by *trans* or vinyl segments, although the differences in the molecular masses of the various grades may also play some role.

FINAL DISCUSSION AND CONCLUSIONS

The reported results can be explained if we take into account that the overall crystallization rate is determined by superpositioning of the rates of crystal nucleation and growth. The process of crystallization of polymers from the melt starts with primary nucleation and then continues with crystal growth and secondary crystallization.[24] Primary nucleation is the process by which crystal nuclei are formed in the melt: nuclei can be formed homogeneously by means of statistical fluctuations or heterogeneously when they are catalyzed by the presence of heterogeneities. After the nuclei are formed, crystalline lamellae develop and form three-dimensional superstructures.

Very often, nucleation of polymers is heterogeneous as heterogeneous nucleation paths make use of foreign existing surfaces to reduce the free energy barrier opposing primary nucleation.[24] The total interfacial free energy of a crystalline embryo is lowered by an external particle that provides part of the interface to be formed; this leads to a reduction in the activation free energy for nucleation and thus in the degree of supercooling required for nucleation. The heterogeneities able to initiate nucleation most often are catalyst remnants or dust particles and the like, but they can also be specifically added particles. In some cases, when no nucleating agents are intentionally added to the material formulation, nucleation can be a rather uncontrolled phenomenon, and considerable variations can be found between batches of the same polymer.[25]

Procedures to eliminate heterogeneities able to initiate crystallization, such as dissolution of the polymer followed by precipitation with pure chemicals, are reported in the literature,[24] but they were not attempted here, being outside the scope of this study. The data reported in Figures 1–5 seem to indicate a main influence of primary nucleation on the crystallization kinetics of the analyzed *cis*-PBD grades. The heterogeneities present in the polymer formulations, either intentionally added or not, are more or less able to initiate the phase transition in the various *cis*-PBD grades, and this process predominates over the kinetics of crystal growth. The onset of the phase transition is determined by the activity of the foreign particles present in each *cis*-PBD grade. In isothermal crystallization, these are responsible for an anticipated beginning of the transition, as quantified in Figure 2, whereas in nonisothermal analysis the effect is seen as a shift of the crystallization exotherms to higher temperature values, as assessed from the data in Figure 4(b). A comparison of the shape of the DSC curves provides further evidence of the different roles played by nucleation and growth in establishing the crystallization rate of the analyzed *cis*-PBD polymers. As shown in Figures 3 and 4(b), the onsets of crystallization of the 95-al and 98-li grades are very close, but in the 95-al grade, the exotherm that developed with the DSC analysis is much broader. This indicates a similar ability of the heterogeneities that are present in the two formulations to promote nucleation, but the slower rate of crystal growth in the 95-al polymer induces crystallization to proceed more slowly. The different effects of nucleation and growth steps are also quantifiable by the higher slope of the 98-li grade at the beginning of the transition, despite the similar undercooling, caused by the faster crystal growth. A comparison of the shapes of the other DSC curves displayed in Figure 3 provides additional evidence. The 97-li and 95-al

grades crystallize in the same temperature range, but the exotherm is narrower for the 97-li polymer because of the higher rate of spherulite growth. The crystallization peak of the 95-al sample is also broader than those of the 97-sb and 98-sb grades, despite the higher undercooling, because of the different rates of crystal growth of the polymers, as shown in Figure 5.

This case study underlines the importance of not limiting an experimental investigation to a single aspect of the problem. Isothermal crystallization studies are generally conducted by an analysis of the bulk crystallization rate that takes into account as the major parameter the half-time of crystallization. Similarly, the main factor considered in nonisothermal crystallization analysis is the peak temperature of the exotherm that develops during the phase transition. In both cases, analysis limited to these values can lead to misleading results about the real crystallization rate, especially upon a comparison of different samples whose crystallization rates may be affected by uncontrollable external factors. The (possibly accidental) introduction into a polymer formulation of foreign particles that may act as nucleating agents and initiate the phase transition is discussed in this contribution for the analyzed PBD grades. A mere analysis of peak position or of the bulk crystallization rate may lead to an erroneous interpretation of the effects of molecular parameters on the crystallization kinetics of *cis*-PBD. It is only with a complete examination of the various contributions to the overall crystallization rate, including the nucleation and crystal growth steps, that eventual spurious effects can be identified and properly separated from the real kinetic data.

References

1. Pires, N. M. T.; Ferreira, A. A.; de Lira, C. H.; Coutinho, P. L. A.; Nicolini, L. F.; Soares, B. G.; Coutinho, F. M. B. J Appl Polym Sci 2006, 99, 88.
2. Boor, J., Jr. Ziegler–Natta Catalysts and Polymerizations; Academic: New York, 1979.
3. Porri, L.; Giarrusso, A. In Comprehensive Polymer Science: The Synthesis, Characterization, Reactions and Applications of Polymers; Eastmond, G. C., Ed.; Pergamon: New York, 1989; Chapter 4.
4. Young, R. N.; Quirk, R. P.; Fetters, L. J. Adv Polym Sci 1984, 56, 1.
5. Makovetskii, K. L.; Yakovlev, V. A.; Golenko, T. G.; Bondarenko, G. N. Polym Sci Ser B 2006, 48, 61.
6. Quirk, R. P.; Kells, A. M.; Yunlu, K.; Cuif, J. P. Polymer 2000, 41, 5903.
7. De Chirico, A.; Lanzani, P. C.; Raggi, E.; Bruzzone, M. Makromol Chem 1974, 175, 2029.
8. Cheng, T. L.; Su, A. C. Macromolecules 1993, 26, 7161.
9. Cheng, T. L.; Su, A. C. Polymer 1995, 36, 73.
10. Miller, J. C. Polymer 1967, 8, 369.
11. Nakajima, N.; Yamaguchi, Y. J Appl Polym Sci 1996, 61, 1525.
12. Cesari, M.; Perego, G.; Zazzetta, A.; Gargani, L. Makromol Chem 1980, 181, 1143.
13. Saijo, K.; Zhu, Y. P.; Hashimoto, T.; Wasiak, A.; Brzostowski, N. J Appl Polym Sci 2007, 105, 137.
14. Di Lorenzo, M. L. Prog Polym Sci 2003, 28, 663.
15. Wunderlich, B. Thermal Analysis; Academic: New York, 1990.
16. Righetti, M. C.; Munari, A. Macromol Chem Phys 1997, 198, 363.
17. Hay, J. N.; Mills, P. J. Polymer 1982, 23, 1380.
18. Cruz-Pinto, J. J.; Martins, J. A.; Oliveira, M. J. Colloid Polym Sci 1994, 272, 1.
19. Righetti, M. C.; Di Lorenzo, M. L.; Angiuli, M.; Tombari, E.; La Pietra, P. Eur Polym J 2007, 43, 4726.
20. de Gennes, P. G. Scaling Concepts in Polymer Physics; Cornell University Press: Ithaca, NY, 1979.
21. Hay, J. N.; Zhou, X. Q. Polymer 1993, 34, 1002.
22. Mathot, V. B. F. In Calorimetry and Thermal Analysis of Polymers; Mathot, V. B. F., Ed.; Hanser/Gardner: Cincinnati, OH, 1994.
23. Di Lorenzo, M. L.; Silvestre, C. Prog Polym Sci 1999, 24, 917.
24. Wunderlich, B. Macromolecular Physics; Academic: New York, 1976; Vol. 2.
25. Binsbergen, F. L. Polymer 1970, 11, 253.