Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 8157–8161

polymer

www.elsevier.com/locate/polymer

In situ optical microscope study of the shear-induced crystallization of isotactic polypropylene

Chenggui Zhang[a,b], Haiqing Hu[a,b,c], Dujin Wang[a], Shouke Yan[a], Charles C. Han[a,*]

[a]*State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*
[b]*Graduate School of Chinese Academy of Sciences, Beijing 100080, China*
[c]*College of Polymer Science and Technology, Qingdao University of Science and Technology, Qingdao 266042, China*

Received 23 March 2005; received in revised form 17 June 2005; accepted 21 June 2005
Available online 25 July 2005

Abstract

The shear-induced crystallization behavior of isotactic polypropylene (i-PP) has been investigated by in situ optical microscope under various thermal and shear histories. A shish-kebab structure during growth was observed under a well controlled, however, weak shear field. According to our results under these weak shear and thermal history, a modified model was proposed for the growing process of melt shear-induced crystallization of i-PP. Furthermore, many physical insights were provided on several still unsettled issues such as extended chain crystals, row nuclei, and smectic ordering questions.

Keywords: Polypropylene; Crystallization; Shish-kebab

1. Introduction

In most polymer processing operations such as injection molding, film blowing, and fiber spinning, the molten polymer chains are subjected to intensive shear and elongational flow fields. It is known that processing conditions profoundly influence the rate of solidification, the semicrystalline morphology, and ultimately material properties [1–3]. The semicrystalline morphology (shish-kebab structure) that developed under shear field [4,5] is typically very different from what is observed under quiescent conditions. It is generally believed that polymer chains are oriented and stretched by the shear flow and can crystallize with different kinetics and consequently different morphologies. Although shear flow is often considered as a ‘weak’ flow, however, it does affect the overall crystallization kinetics [6–9] and modify the final morphologies and properties [9–12] of polymeric materials. In recent years, studies of flow-induced crystallization have drawn a lot of interests because it reveals the possibilities of controlling and predicting the final morphologies and properties of the semicrystalline polymers in most of the transformation processes, meanwhile, provided an opportunity to understand some fundamental issues among molecular conformations, ordering processes, as well as nucleation and crystallization kinetics [1,13–15].

In this communication, we present some results of in situ optical microscopy studies of shear-induced crystallization of isotactic polypropylene melts under various thermal and shearing histories. It directly revealed the lamellar growth process occurred from an oriented long shish structure. These fibril like shish structure, the perpendicular lamellar growth geometry, as well as the beta-formation and its melting behavior can provide many physical insights on several still unsettled issues such as extended chain crystals, row nuclei, and smectic ordering [14,15] questions. More detailed scattering studies are still underway in our laboratory.

2. Experimental details

The isotactic polypropylene homopolymer was provided

---

[*] Corresponding author. Tel.: +86 10 8261 8089; fax: +86 10 6252 1519.
E-mail address: c.c.han@iccas.ac.cn (C.C. Han).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.06.074

by Yanshan Petrochemical Corp., Inc. The molecular weights of i-PP resin, as obtained from the GPC experiments, are $M_n = 9.62 \times 10^4$, $M_w = 4.38 \times 10^5$ with a polydispersity $D = 4.55$.

A Linkam CSS-450 high-temperature shearing stage (Linkam Scientific Instruments Ltd, Tadworth, Surrey, UK), and an optical microscope (Nikon E600POL) were used in this study. The mechanical design and electronic control of the Linkam shear stage provided adequate conditions for the present experiments, such as the sample thickness, temperature, shear rate and heating/cooling rate. In recent years, this model of apparatus has been used for investigating the shear-induced crystallization of polymers in many research works [8,13–16].

In our experiments, steady shear mode was selected. The gap between the windows was 20 μm. The experiment procedure was chosen as follows: (1) Heating at 30 °C/min from room temperature to 200 °C; (2) annealing at 200 °C for 5 min to eliminate all possible residual structure; (3) cooling at a rate of 30 °C/min down to 140 °C; (4) the samples were immediately sheared at 140 °C for 5 s; (5) after shear cessation, the samples were isothermally crystallized at 140 °C and the microscope photos were taken in situ by a CCD camera (Nikon Coolpix4500). The optical characteristic, i.e. the sign of birefringence of the micromorphologic feature was determined by means of a primary red filter (λ-plate) located diagonally between cross polarizers.

3. Results and discussion

Fig. 1 shows the polarized optical micrographs of i-PP samples sheared at a rate of 0.5 s^{-1}. Classical 'shish-kebab' morphologies are clearly observed. The landscape orientation of lamellae run perpendicular to the narrow backbone as the kebab structure should be. The structure is in close resemblance to the polymorphic shish-kebab morphology in PP melts sheared with fibers [6,7,11,12], crystallization in fibers/polymer composites [17–19], or sample crystallization by a razor blade shear in the melt [20], however, in our experiment there is neither fibers nor other nucleation species were used. Recently, Pogodina [21], Sharama [22] and Hsiao [23] studied flow induced crystallization. The shish-kebab structure were observed at high shear rates, at weak shear conditions (below 1 s^{-1}), only continuous nucleation were found. To the best of our knowledge, this is the first real space observation of a shish-kebab structure during growth with a well controlled weak shear field (shear rate below 1 s^{-1}) and without further shear destruction of such a structure. It is obvious from our observation that when i-PP melt was subjected to shear, either molecular chains or short helical segments are oriented and aligned along the flow direction [1,4,5]. After shear stopped, the oriented i-PP molecular chains or row nuclei served as sites for either an epitaxial primary nucleation growth or may be for a secondary nucleation and growth.

In Fig. 2, observations similar to that of Fig. 1 were displayed, except that the shear rate was doubled to 1 s^{-1}. It is obvious that the major difference is the number of rows or fibrils formed by the shear flow is larger, consequently the number of nuclei and the overall crystallization rate. The remaining features are similar to those in Fig. 1.

It is generally known that the fraction of β-form crystal increases with shear rate [24] for i-PP under transformation. The β-form of i-PP demonstrates different performance characteristics, including improved elongation at break and impact strength [25,26]. It can be obtained by some special techniques such as with the addition of certain heterogeneous nucleating agents [27], the crystallization in a temperature gradient [28], or the shear-induced crystallization [11,12,24]. The polarized optical micrographs consisting of shish-kebab structure and α-spherulite are shown in Fig. 3(a), where a mixed polymorphic structure ($\alpha + \beta$) is displayed. The β-spherulite which originated from and attached to the oriented folded chain lamellae/crystals or kebabs was probably formed through the growth transformation from the oriented α-front [11,28]. This β-form in the specimen can be selectively melted out by heating the sample from T_c to 156 °C. Then only the α-crystalline region remained in the specimen (Fig. 3(b)).

The amount of β-form is small in our experiment, probably due to the low shear rate (1 s^{-1}) used [16].

When the polymer melt was subjected to shear, it is natural that the polymer chain in the melt is extended along the flow direction and forms extended micro-fibril-like structures, provided that the shear rate is higher than the longest relaxation rate of a single chain or the disentanglement rate of multiple polymer chains. In our system we know that the i-PP forms entangled network, with molecular weight much larger than the average molecular weight (of i-PP) between entanglements coupling point, M_e. The shear rate for Newtonian to non-Newtonian transition (or network deformation) happens at around 100 s^{-1} [29], which is much higher than the shear rate for our shish-kebab formation. Therefore, we think the entangled network we are dealing with must be further immobilized by some fixed points (in terms of time scale which must be longer than our shear time) at the entanglement junctions in our experimental conditions. These fixed junction points do not need to be permanently fixed, such as covalent bonding or permanent crystallite. As long as the relaxation time (or dissipation time) of these junction points are longer than our shear time (inverse shear rate), which will be sufficient to cause the network deformation and the chain bundle formation. Therefore, we propose that either some fluctuating helical structure or some crystal embryo could have formed at the entangled junction points. These junction points, temporary may be, may have already formed at the temperature and shear rate of our experimental conditions which allows the stretch of a bundle of chains which may be

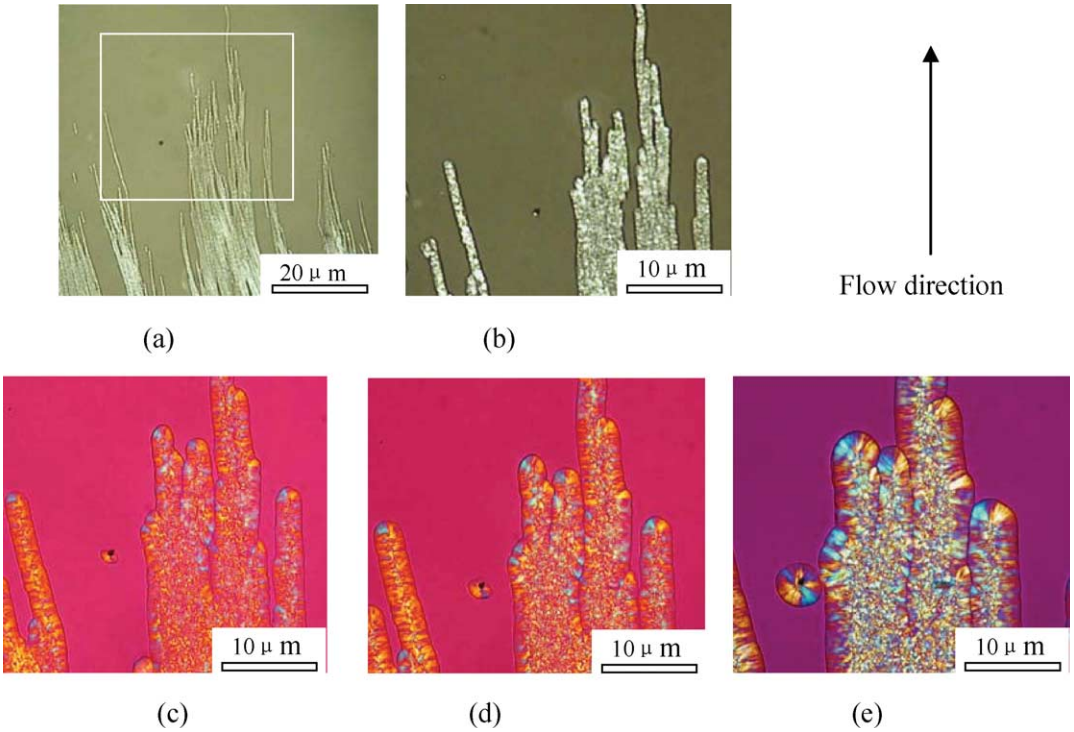


Fig. 1. Optical micrographs of i-PP. i-PP melted at 200 °C for 5 min, then quenched to 140 °C and sheared 5 s at the shear rate $= 0.5\ \mathrm{s}^{-1}$. After shear cessation, the samples were isothermally crystallized at 140 °C for (a) 142 s, (b) 419 s, (c) 865 s, (d) 1093 s, (e) 1784 s; (a) and (b) are the polarized micrographs, (c)–(e) are taken by means of a primary red filter (λ-plate); (b)–(e) show the white box part of (a).

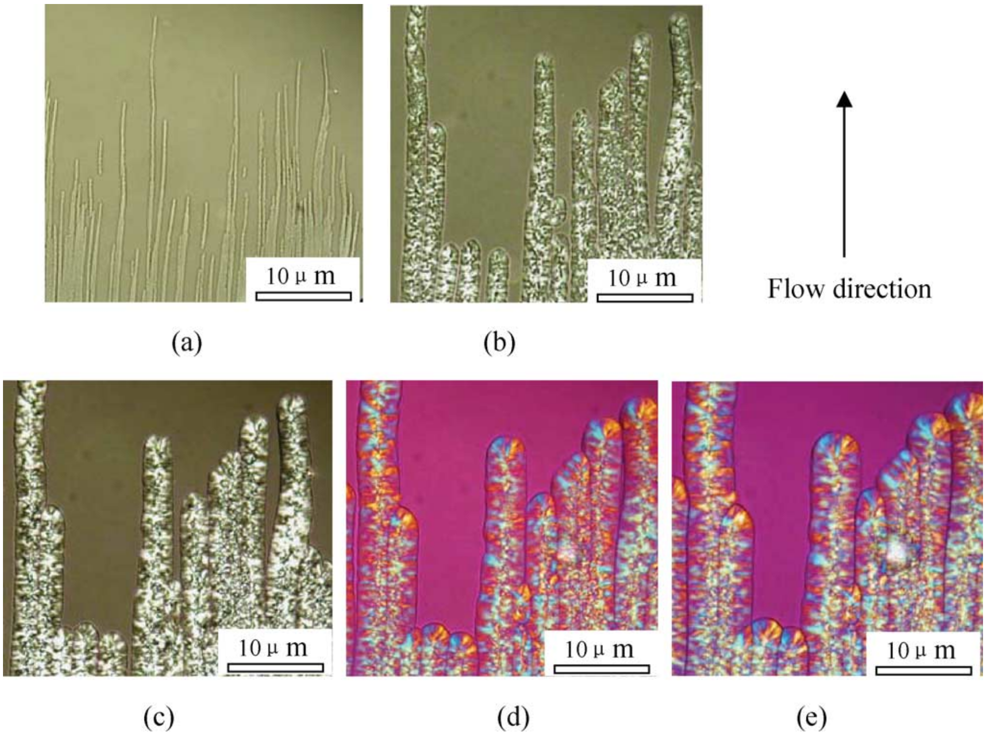
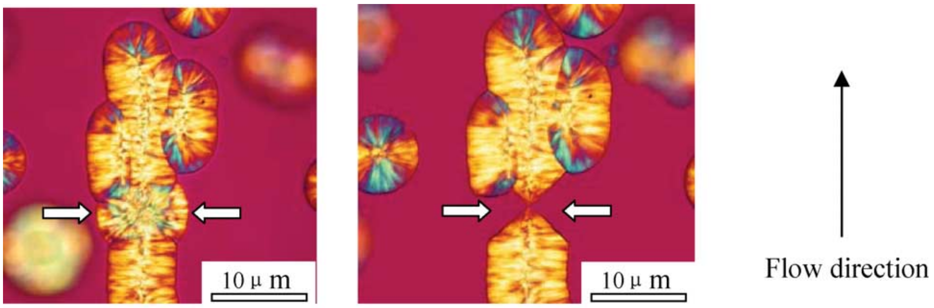


Fig. 2. Optical micrographs of i-PP. i-PP melted at 200 °C for 5 min, then quenched to 140 °C and sheared 5 s at the shear rate $= 1\ \mathrm{s}^{-1}$. After shear cessation, the samples were isothermally crystallized at 140 °C for (a) 160 s, (b) 603 s, (c) 958 s, (d) 1320 s and (e) 1660 s; (a)–(c) were the polarized micrographs; (d) and (e) were by means of a primary red filter (λ-plate).



(a) (b)

Fig. 3. Cross-polarized optical micrographs of β-form i-PP crystal by shearing i-PP melt at 134 °C, shear rate = 1 s^{-1}; (a) i-PP melted at 200 °C for 5 min, then quenched to 134 °C and sheared 5 s at the shear rate = 1 s^{-1}, followed by isothermally crystallization for 500 s (contents both α and β forms); (b) The selective melting of the β-form at 156 °C, the arrows point to the β forms.

consequently grow into the extended chain crystal shish or a liquid crystalline like ordered shish structure (we cannot distinguish the two possibilities in our optical microscopic observation, and we cannot make preference with the current experiments).

A low shear rate, such as 1 s^{-1} is enough to deform and stretch the network chains and align the chains together with the helical segment (or crystal embryo) into extended form or row form. Furthermore, the stretch induced order at a temperature below the melting temperature (e.g. 140 °C) could possibly induce the transformation of the helical segments into a smectic ordered liquid crystalline (LC) structure [14,15] or a row nuclei structure with a nanometer length correlation-length.

Although we cannot distinguish directly the stretched polymer chain bundles which may be further crystallized into extended crystals, from the row nuclei with polymer chain bundle in between, or from smectic ordering as suggested in Refs. [14,15], however, from the low shear rate response and the PLM pictures of our experiments, we believe the row nuclei model is the more realistic one. The SAXS peaks observed in Refs. [14,15] are not necessarily coming from a smectic ordered shish. The SAXS peak in the reciprocal nanometer range merely reflected that a preferred correlation length of nanometer does exist. We suggest that this preferred nanometer dimension could come from, M_e, the strand molecular weight between entanglement coupling points. Suppose we have a string of row nuclei coming from the crystal embryo initiated at the entanglement points, then these string of nuclei will be naturally separated by a distance distributed around the average length of M_e, which is about 10–20 nm (or about 70–100 monomer unites) [29].

Regardless whether there is a smectic order or just a row order with a narrow correlation-length distribution from our experiment, a fibril-like structure is definitely formed which promotes the epitaxial growth of folded chain lamellae and filled the space perpendicular to the flow direction. That results in a cylindrical supra-molecular morphological structure known as 'shish-kebab'. It is obvious from this picture that the high molecular weight, high shear rate and lower crystallization temperature will all promote this effect, as long as the shear strain is not too large (above 200%) to distort the row structures and the transverse crystals formed subsequently.

Somani [13] extended the idea of Keller [30] for elongational flow-induced crystallization to shear flow. At a given shear rate, only molecules with high molecular weight can be oriented. The oriented molecules serve as the precursor or primary nuclei. The molecular weight and its distribution play an essential role. In a polydispersed polymer sample, only the high-molecular weight part contributes to the enhancement of the crystallization rate. They also offered a molecular picture for nucleation and growth induced by transient shearing, which is mediated by the chains above a critical orientation molecular weight. In their results, stacked lamellae oriented perpendicular to the flow direction was observed by TEM, however, the shish structure was never observed under their experimental conditions.

According to our experimental results performed at lower shear rates and in situ, we provide a modified model for the growing process of shear flow-induced crystallization of i-PP in Fig. 4. In our picture, a rod-like structure consists of row nuclei parallel and aligned to flow direction with either a few (or tenth) nanometer correlation-length order or smectic order, is formed by the shear flow through network stretching as demonstrated in Fig. 4(a) and (b). Supposedly an adjacent chain adsorbs to a ordered structure (either a smectic LC or helical crystallite) with a surface normal to the gradient direction, the free segments of such a chain will subsequently crystallize and form the kebab as shown schematically in Fig. 4(c) and (d). After shear cessation, lateral growth continues from the threadlike precursors. Since chain relaxation in the melt occurs quickly after shear cessation, the growing velocity is expected to be similar to that of the quiescent case. With the crystallization time prolonging, the same process can repeat itself over and over again, so the kebab structure becomes larger. Fig. 4(e) shows the final shape of the crystallized samples. This

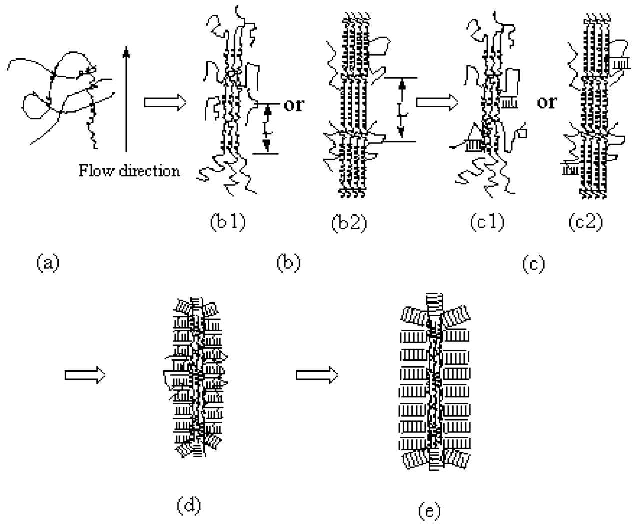


Fig. 4. Schematic illustration of the morphological development during shear-induced crystallization of i-PP: (a) Entangled random coils before shear (amorphous melt, no orientation) with possible helical segments; (b) shear-induced nuclei, (b1) row order nuclei; (b2) smectic order nuclei; (c) and (d) epitaxial growth of shish-kebab, (c1) growth from row ordered nuclei, (c2) growth from smectic ordered structure; (e) final morphology after shear-induced crystallization.

picture is consistent with the simulation works carried out recently by Muthukumar [31] and Hu [32].

4. Conclusion

We have presented in this report an in situ optical microscope study of the crystallization of i-PP under shear with the formation of shish-kebab like α-structure and the growth front induced β-form crystals. According to our results, a modified model has been proposed for the growing process of shear-induced crystallization in i-PP melt.

Although we cannot distinguish smectic liquid crystalline like order from row nuclei alignment with correlation length of the order of the strand molecular length between entanglement coupling points, it is obvious that ordered structure with preferred correlation length does exist [14]. This structure could easily come from the short helical structure (or crystal embryo) existing in the melt (even above the melting temperature of the crystal) [15] at entanglement point and was enhanced during the shearing flow. The shearing flow could naturally have stretched the network and aligned and enhanced the helical segments or clusters and ordered them with a correlation length commensurate with the average molecular weight entanglement coupling point of i-PP in the quiescent melt.

Acknowledgements

This work was supported by three projects: KJCX2-SW-H07, 2003 CB 615600 and 20490220.

References

[1] Odell JA, Grubb DT, Keller A. Polymer 1978;19:617–26.
[2] Bushman AC, McHugh AJ. J Appl Polym Sci 1997;64:2165–76.
[3] Okamoto M, Kubo H, Kotaka T. Macromolecules 1998;31:4223–31.
[4] Pennings J, Kiel AM. ZZ Colloid Polym 1965;205:160.
[5] Pennings J. J Polym Sci, Part C: Polym Symp 1977;59:55–86.
[6] Jay F, Haudin JM, Monasse B. J Mater Sci 1999;34:2089–102.
[7] Duplay D, Monasse B, Haudin JM, Costa JL. J Mater Sci 2000;35:6093–103.
[8] Abuzaina FM, Fitz BD, Andjelic S, Jamiolkowski D. Polymer 2002;43:4699–708.
[9] Kumaraswamy G, Issaian AM, Kornfield JA. Macromolecules 1999;32:7537–49.
[10] Varga J. Angew Makromol Chem 1983;112:191–203.
[11] Varga J, Karger-Kocsis J. J Polym Sci, Part B: Polym Phys 1996;34:657–70.
[12] Wu CM, Chen M, Karger-Kocsis J. Polymer 1999;40:4195–203.
[13] Somani RH, Hsiao BS, Nogales A, Srinivas S, Tsou AH, Sics I, et al. Macromolecules 2000;33:9385–94.
[14] Li LB, Jeu WH. Macromolecules 2003;36:4862–7.
[15] Li LB, Jeu WH. Phys Rev Lett 2004;92:075506/1–075506/3.
[16] (a) Fu BX, Yang L, Somani RH, Zong SX, Hsiao BS, Phillips S, et al. J Polym Sci, Part B: Polym Phys 2001;39:2727–39.
(b) Huo H, Jiang SC, An LJ, Feng J. Macromolecules 2004;37:2478–83.
[17] Li HH, Jiang SD, Wang J, Wang D, Yan SK. Macromolecules 2003;36:2802–7.
[18] Wang C, Liu CR. J Polym Sci, Polym Phys Ed 1998;36:1361–70.
[19] Gaceva BG, Janevski A, Mader E. Polymer 2001;42:4409–16.
[20] Hobbs JK, Humphris ADL, Miles MJ. Macromolecules 2001;34:5508–19.
[21] Pogodina NV, Lavrenko VP, Srinivas S, Winter HH. Polymer 2001;42:9031–43.
[22] (a) Sharma L, Ogino Y, Kanaya T. Macromol Mater Eng 2004;289:1059–67.
(b) Sharma L, Ogino Y, Kanaya T, Iwata T, Doi Y. Macromol Mater Eng 2004;289:1068–73.
[23] Hsiao BS, Yang L, Somani RH, Avila-Orta CA, Zhu L. Phys Rev Lett 2005;94:117802/1–117802/4.
[24] Somani RH, Hsiao BS, Nogales A, Fruitwala H, Srinivas S, Tsou AH. Macromolecules 2001;34:5902–9.
[25] Huang M, Li XG, Fang BR. J Appl Polym Sci 1995;56:1323–37.
[26] Zhu PW, Edward G. Marcromol Mater Eng 2003;288:301–11.
[27] Stocker W, Schumacher M, Graff S, Thierry A, Wittmann JC, Lotz B. Macromolecules 1998;31:807–14.
[28] Lovinger AJ, Chua JO, Gryte CC. J Polym Sci, Part B: Polym Phys 1977;15:641–56.
[29] Ferry JD. Viscoelastic properties of polymers. New York: Wiley; 1980.
[30] Pope DP, Keller A. Colloid Polym Sci 1978;256:751–6.
[31] Dukovski I, Muthukumar M. J Chem Phys 2003;118:6648–55.
[32] Hu W, Frenkel D, Mathot VBF. Macromolecules 2002;35:7172–4.