

NOTE

Crystalline layered morphology in the phase-separated blend of poly(butylene succinate) and poly(ethylene succinate)

Toshiyuki Kataoka, Toshitaka Abe and Takayuki Ikehara

Polymer Journal (2015) 47, 645–648; doi:10.1038/pj.2015.46; published online 24 June 2015

INTRODUCTION

Crystalline/crystalline polymer blends that are binary systems that consist of a crystalline polymer pair have received increasing attention in recent decades because they show various crystalline morphology and crystallization processes.^{1–20} One of the intriguing phenomena in crystalline/crystalline blends is the formation of interpenetrating spherulites; namely, the spherulites of one component that continue to grow inside those of the other component.^{7,9,10,13–17} If the difference in the melting temperature (T_m) between the two crystalline constituents is smaller than ~ 30 K, both components simultaneously nucleate in the melt to form interpenetrating spherulites.^{14,15} For a larger T_m difference,^{2,7,13,17} the spherulites of the higher T_m component nucleate first and fill the entire volume. Then, the lower T_m component crystallizes inside the spherulites of the higher T_m component while maintaining the original shape of the pre-existing spherulites.

Poly(butylene succinate) (PBS) and poly(ethylene succinate) (PES) are crystalline polyesters, and they are immiscible with each other in a wide composition range.^{11,12,16,18} In our previous work on PBS/PES blends using polarized optical microscopy (POM),¹² the PBS spherulites, which nucleated first in the PBS-rich phase, continued to grow across the phase boundaries between the PBS- and PES-rich phases at the temperature where only PBS crystallizes. The PBS spherulites maintained a spherical shape even in the heterogeneous melt. This result indicated that the growth rates in the PBS- and PES-rich phases are identical despite the large difference in composition between them. When the blend was further quenched, the PES spherulites developed in the PES-rich phase, where PES appeared to form interpenetrating spherulites with PBS. However, the spherulitic morphology in the PES-rich phase was different from the original shape of the PBS spherulites after the crystallization of PES.

In the previous study,¹² the formation of PBS-rich layers on the PES-rich phases was assumed to explain such results. However, these layered structures are not usually formed in phase-separated blends, and the spherulitic growth terminates at the phase boundaries.^{5,8,10}

The layered morphology of the PBS/PES blends was discussed to be stabilized by copolyesters, which were formed by transesterification between PBS and PES in the melt.¹² These stable layers that are spontaneously formed in binary blends are intriguing structures that can control the surface properties such as friction and adhesion. Nevertheless, direct evidence for the existence of the layered structure has not been obtained.

In the present note, the surface morphology of a PBS/PES blend was studied using atomic force microscopy (AFM) to obtain detailed information on the layered structures in the crystalline/crystalline system of PBS and PES. Before the AFM investigations, the blend film was first crystallized at the crystallization temperature (T_c) of PBS and successively at the T_c of PES, and the crystallization process was observed using POM. The layered structure in the phase-separated blend was discussed based on the morphology, which was observed using AFM and optical microscopy.

EXPERIMENTAL PROCEDURE

PBS ($M_w = 83\,000$, $T_m = 120$ °C) and PES ($M_w = 10\,000$, $T_m = 108$ °C) were purchased from Sigma-Aldrich Corporation (St Louis, MO, USA) and Scientific Polymer Products (Ontario, NY, USA), respectively. The PBS and PES with the weight ratio of 4/6 were dissolved in chloroform. The solution was spin-coated at 750 r.p.m. for 15 s on an optical glass substrate for several times. The blend film with a thickness of ~ 10 μm was obtained after it was dried *in vacuo* at 40 °C for 2 days.

The crystallization process was observed using a polarized optical microscope (BX51, Olympus Corporation, Tokyo, Japan), which was equipped with a sensitive tint plate with a retardation of 530 nm, a temperature controller (LK-600PM, Linkam, Surrey, UK), and a charge-coupled device (CCD) camera (Micropublisher 5.0, QImaging, Surrey, BC, Canada). The blend film that was mounted on the microscope was melted at 150 °C and immediately cooled to 80 °C, where only PBS crystallized. The PBS spherulites filled the micrograph when the temperature was maintained for ~ 10 min. Then, the blend was further cooled to 50 °C to crystallize PES.

The AFM observation was performed using a Nanoscope V (Bruker Corporation, Billerica, MA, USA) instrument with a silicon probe (Olympus

Corporation, OMCL-AC160TS-R3). After the blend film was crystallized on the optical microscope as previously mentioned, arrows were drawn on the edge of the sample to indicate the observed area. The location that was observed using POM was determined based on the drawn arrows using a stereo microscope (Olympus Corporation, SZ-ST5), which was equipped on the AFM stage. The sample was scanned in the tapping mode at room temperature.

Water contact angle measurements were conducted with a contact angle meter (SImage mini 7, Excimer, Yokohama, Japan). The films of PBS and PES were prepared by melt pressing. Deionized water (4 μ l) was dropped on the polymer film at room temperature and photographed using a CCD camera. The contact angle values, which were obtained at different points, were averaged for each film.

RESULTS AND DISCUSSION

The phase contrast microscopy observation shows that the blends of PBS/PES = 4/6 were phase-separated immediately above the T_m of PBS.¹² The crystallization process of the PBS/PES blend is shown in Figure 1. When the phase-separated melt was quenched to 80 °C, compact PBS spherulites nucleated (Figure 1a). The brighter and darker parts of the spherulites are in the PBS- and PES-rich phases, respectively, because PES spherulites were formed in only the darker parts, as described later. The PBS spherulite S_1 , which nucleated in the PBS-rich phase, continued growing across interface I_1 between the PBS- and PES-rich phases. The impingement of the growth front of S_1 on another PBS spherulite S_2 resulted in the formation of the spherulitic boundary B_1 in the PES-rich phase (Figure 1b). PES spherulites were formed in only the PES-rich phase after the blend was further quenched to 50 °C (Figure 1c). The PES spherulite S_3 grew

across boundary B_1 of the PBS spherulites. After the PES crystallization completed, the radial directions and boundaries of the PBS spherulites in the PES-rich phase became unclear (Figure 1d).

The indistinct spherulitic morphology of PBS in the PES-rich phase in Figure 1d suggests that PES and PBS have different lamellar growth directions. This result implies that PES crystallized outside the PBS spherulites. However, in miscible blends of PBS with poly(ethylene oxide),² the original spherulitic shapes of PBS were maintained when poly(ethylene oxide) spherulites grew inside the PBS spherulites. This result is ascribed to the identical growth directions of PBS and poly(ethylene oxide) lamellae.² Other miscible crystalline/crystalline blends also show similar behaviors.^{2,10,13,15}

The radius of the PBS spherulite S_1 against the crystallization time is shown in Figure 2. Although S_1 grew across the phase interface I_1 , the radius exhibits a linear relationship with the crystallization time. This result indicates that the growth rate in the PES-rich phase is identical with that in the PBS-rich phase despite the large difference in blend composition between the two phases. It is noted that a blend with a higher concentration of the crystallizing component usually shows a faster spherulitic growth rate.²¹

The surface morphology of the PBS/PES blend after the successive crystallization of PBS and PES was investigated using AFM. Figure 3a shows the height image of the squared region in Figure 1d. The left- and right-hand sides of Figure 3a correspond to the surfaces of the PES- and PBS-rich phases, respectively. The spherulitic boundary B_1 in Figure 1b is observed in the upper part of Figure 3a, although B_1 in the

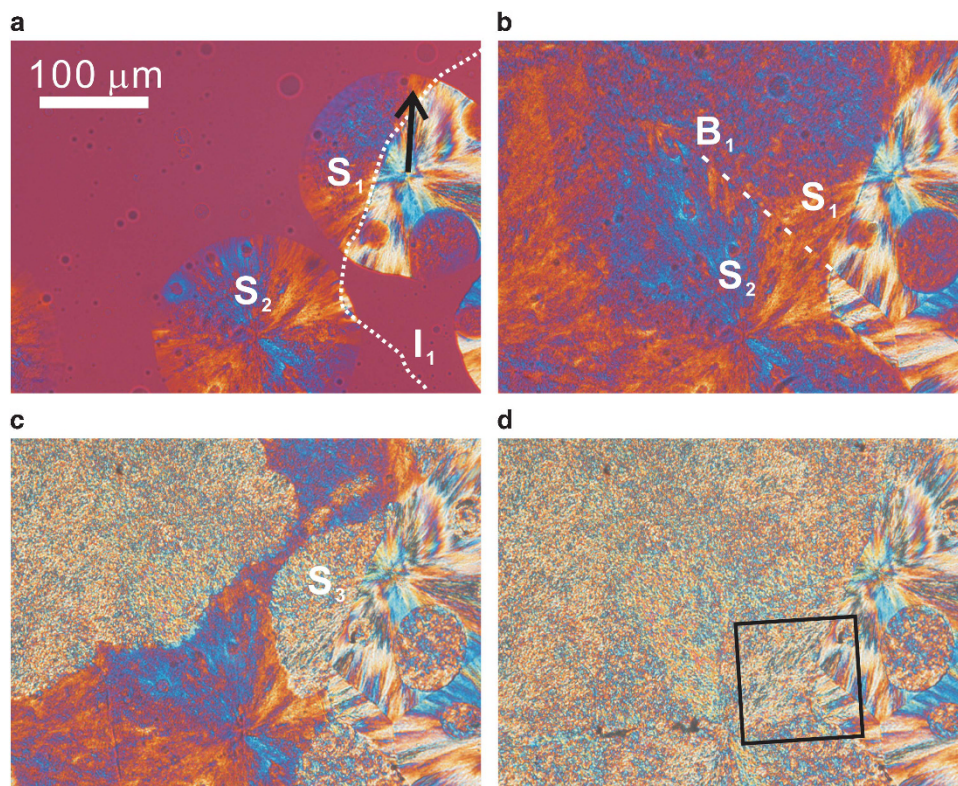


Figure 1 Polarized optical micrographs of the spherulitic growth in the blend of PBS/PES = 4/6. (a) The growth of PBS spherulites (S_1 and S_2) in the phase-separated melt at 80 °C. The dotted line I_1 denotes the interface between the PBS- and PES-rich phases. The spherulitic radius in the direction of the arrow is shown in Figure 2. (b) Completion of the spherulitic growth of PBS 8 min after (a). The dotted line B_1 denotes the spherulitic boundary between S_1 and S_2 . (c) Nucleation and growth of PES spherulites at 50 °C. S_3 indicates the PES spherulite that grew across B_1 . (d) Completion of the spherulitic growth of PES 12 min after (c). The AFM image in the squared region is shown in Figure 3a.

PES-rich phase was not detected by POM after the growth of PES crystals, as shown in Figure 1d.

The enlarged image of the upper part of Figure 3a is shown in Figure 3b, which corresponds to the image around boundary B_1 in the PES-rich phase. Figures 3c and d show the height profiles along the lines in Figure 3b. The surface was concave toward boundary B_1 (Figure 3c). There are ridges that are almost perpendicular to B_1 , as indicated by triangles 2–4 in Figures 3b and d. The orientation directions of these ridges were identical to the growth directions of the PBS spherulites S_1 and S_2 (dashed arrows in Figure 3a). However, Figure 3 shows no structures attributable to the PES spherulite S_3 , which nucleated as in the upper-right part of Figure 3a and grew radially as shown in Figure 1c. Therefore, the surface image of the

PES-rich phase, which was obtained using AFM, coincides with the spherulitic morphology of PBS in Figure 1b, although the spherulitic shape of PBS in the PES-rich phase that was observed using POM became indistinct after the PES crystallization.

The results obtained by AFM and POM were compared; the comparison indicates that a thin layer of the PBS-rich phase is located on the PES-rich phase as illustrated in Figure 4a. The constant growth rate of the PBS spherulite in the heterogeneous melt in Figure 2 also indicates the existence of PBS-rich layers, through which the PBS spherulites continuously grew. One possible reason for the preferential presence of the PBS-rich phase at the air interface is the difference in hydrophobicity between PBS and PES. The water contact angles of PBS and PES were 66° and 46° , respectively, which suggests that PBS is a more hydrophobic polymer than PES. The difference in hydrophobicity between PBS and PES must originate from the length of a hydrophobic alkyl group in the repeating unit (Figure 4b).

The PBS layer may also have been formed between the PES-rich phase and the glass substrate because the PBS/PES blends between two glass substrates also showed the continuous growth of PBS in the PES-rich phase.¹² Both before and after etching in KOH/ethanol solution, the glass substrates were used in these observations. Although the exact reason for the formation of the PBS-rich layer on the hydrophilic glass substrate cannot be determined from this study, strong adsorption of the polymers onto the glass surface^{22,23} may have changed the wettability of the substrate.

However, in the studies of crystalline/crystalline blends,^{5,8,10} the phase-separated blends did not show such layered structures; the spherulitic growth in the biphasic melt stopped at the phase boundaries. The layered morphology has a larger interfacial area than the laterally segregated structure in a phase-separated thin film. The laterally segregated structure should be more stable than the layered structure because a smaller interfacial area generally results in lower free energy. However, transesterification occurs in the melts of PBS/PES blends and forms PBS–PES block copolyesters via exchanging the main chains (Figure 4c).¹² The change in molecular weight

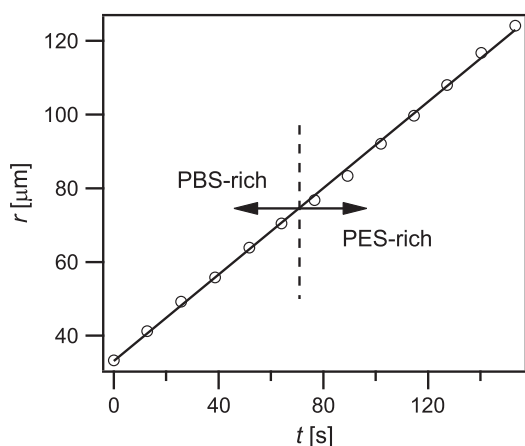


Figure 2 Time dependence of the radius r of the PBS spherulite S_1 in the direction of the arrow in Figure 1a. The dashed line indicates the time when the growth front reaches interface I_1 between the PBS- and PES-rich phases.

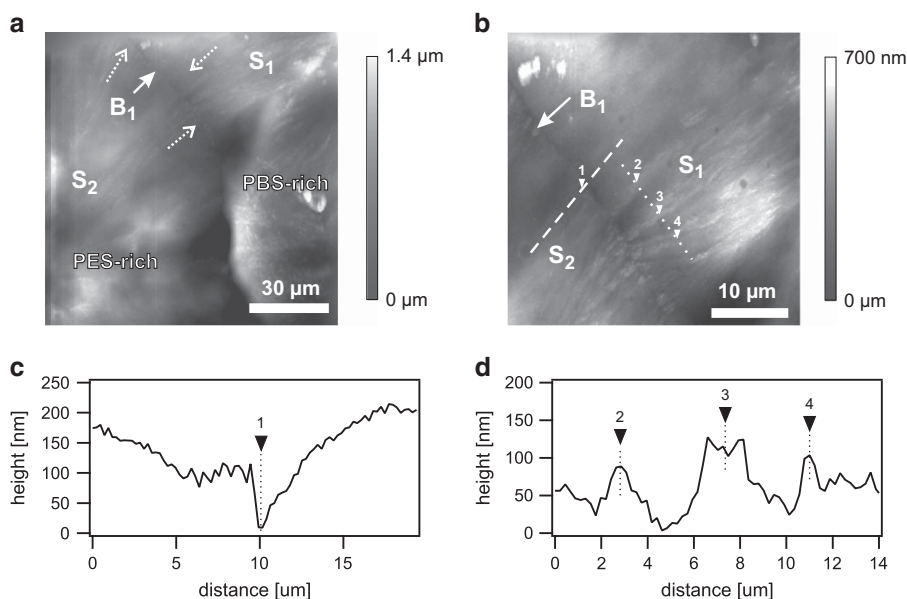


Figure 3 AFM images of the blend of PBS/PES = 4/6 after crystallization. (a) Height image of the squared region in Figure 1d. The dashed arrows indicate the growth directions of PBS spherulites S_1 and S_2 . (b) Enlarged view of the PES-rich phase at the upper part of (a). Height profiles along the (c) dashed and (d) dotted lines in (b). The points that are indicated by the triangles in (b) are shown in (c) and (d).

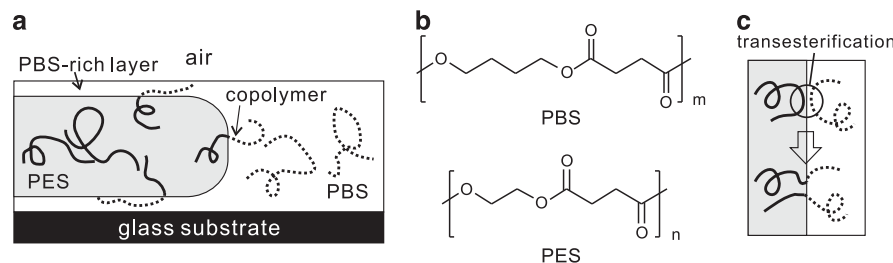


Figure 4 (a) Schematic illustration of the phase morphology of the PBS/PES blend in the melt. (b) Chemical structures of PBS and PES. (c) Illustration of the formation of PBS-PES copolymers through transesterification at the interface between PBS- and PES-rich phases.

distribution of the PBS/PES blend was detected using gel permeation chromatography after annealing for only 5 min at 150 °C, which is immediately above the T_m of PBS (see Supplementary Figure S1 in Supplementary Information). The thermal decomposition of PBS and PES in an inert atmosphere was negligible because the chromatograms of the annealed blends have no signs that indicate the existence of low-molecular weight molecules. This result indicates that transesterification between PBS and PES occurs rapidly in the melt, and a small amount of copolyesters should have formed in the blend during the heating and cooling processes of the melt crystallization. The formation of copolyesters, which preferentially localize at the interface between the two phases as shown in Figure 4a, can decrease the surface free energy and stabilize the layered morphology.

CONCLUSIONS

The surface morphology of the phase-separated blend of PBS and PES was investigated with AFM to obtain direct evidence of the crystalline layered structure. When the melt was quenched to the T_c of PBS, PBS spherulites that nucleated in the PBS-rich phase continuously grew into the PES-rich phase at an identical growth rate. The spherulitic shape of PBS in the PES-rich phase became unclear after PES was crystallized by further quenching. The surface structures that were obtained using AFM indicate that a PBS-rich layer was formed between air and the PES-rich phase. The existence of the PBS-rich layer can explain the continuous crystallization of PBS into the PES-rich phase and constant spherulitic growth rate of PBS in the heterogeneous melt. A small amount of PBS-PES copolymers must have been formed through rapid transesterification between PBS and PES during the melt crystallization. The stable layered morphology can be partly attributed to the localization of copolymers between the two phases.

ACKNOWLEDGEMENTS

This work was partly supported by a Grand-in-Aid for Scientific Research (C) from Japan Society for the Promotion of Science (26410228) and by the MEXT (Ministry of Education, Culture, Sports, Science and Technology)—Supported Program for the Strategic Research Foundation at Private Universities, 2013–2017.

- Kabe, T., Sato, T., Kasuya, K., Hikima, T., Takata, M. & Iwata, T. Transition of spherulite morphology in a crystalline/crystalline binary blend of biodegradable microbial polyesters. *Polymer* **55**, 271–277 (2014).
- Ikehara, T., Kurihara, H. & Kataoka, T. Effect of poly(butylene succinate) crystals on spherulitic growth of poly(ethylene oxide) in binary blends of the two substances. *J. Polym. Sci. B Polym. Phys.* **47**, 539–547 (2009).

- Chen, Z. G., Zhou, T., Hui, J. T., Li, L., Li, Y. Y., Zhang, A. M. & Yuan, T. Y. Tracing the crystallization process of polyoxymethylene/poly(ethylene oxide) crystalline/crystalline blends by two-dimensional infrared correlation spectroscopy. *Vib. Spectrosc.* **62**, 299–309 (2012).
- Zeng, J. B., Zhu, Q. Y., Li, Y. D., Qiu, Z. C. & Wang, Y. Z. Unique Crystalline/crystalline polymer blends of poly(ethylene succinate) and poly(*p*-dioxanone): miscibility and crystallization behaviors. *J. Phys. Chem. B* **114**, 14827–14833 (2010).
- Qiu, Z. B., Ikehara, T. & Nishi, T. Miscibility and crystallization behaviour of biodegradable blends of two aliphatic polyesters. Poly(3-hydroxybutyrate-co-hydroxyvalerate) and poly(butylene succinate) blends. *Polymer* **44**, 7519–7527 (2003).
- Zhao, L. F., Peng, X. Y., Liu, X., Wang, Y. M., Qin, S. X. & Zhang, J. Miscibility and morphology of binary crystalline blends of poly(L-lactide) and poly(butylene adipate). *Polym. J.* **45**, 929–937 (2013).
- Wang, T. C., Li, H. H., Wang, F., Yan, S. K. & Schultz, J. M. Confined growth of poly(butylene succinate) in its miscible blends with poly(vinylidene fluoride): morphology and growth kinetics. *J. Phys. Chem. B* **115**, 7814–7822 (2011).
- Qiu, Z. B., Komura, M., Ikehara, T. & Nishi, T. Miscibility and crystallization behavior of biodegradable blends of two aliphatic polyesters. Poly(butylene succinate) and poly(ϵ -caprolactone). *Polymer* **44**, 7749–7756 (2003).
- Qiu, Z. B., Fujinami, S., Komura, M., Nakajima, K., Ikehara, T. & Nishi, T. Structure and properties of biodegradable polymer-based blends. *Macromol. Symp.* **216**, 255–263 (2004).
- Qiu, Z. B., Yang, W. T., Ikehara, T. & Nishi, T. Miscibility and crystallization behavior of biodegradable blends of two aliphatic polyesters. Poly(3-hydroxybutyrate-co-hydroxyvalerate) and poly(ϵ -caprolactone). *Polymer* **46**, 11814–11819 (2005).
- He, Y. S., Zeng, J. B., Li, S. L. & Wang, Y. Z. Crystallization behavior of partially miscible biodegradable poly(butylene succinate)/poly(ethylene succinate) blends. *Thermochim. Acta* **529**, 80–86 (2012).
- Kataoka, T., Hiramoto, H., Kurihara, H. & Ikehara, T. Effects of melt annealing on the miscibility and crystallization of poly(butylene succinate)/poly(ethylene succinate) blends. *Polym. J.* **46**, 405–411 (2014).
- Ikehara, T., Kurihara, H., Qiu, Z. & Nishi, T. Study of spherulitic structures by analyzing the spherulitic growth rate of the other component in binary crystalline polymer blends. *Macromolecules* **40**, 8726–8730 (2007).
- Ikehara, T., Kurihara, H. & Kataoka, T. Spherulitic growth in block copolymers and blends of miscible crystalline polymers. *J. Polym. Sci. B Polym. Phys.* **50**, 563–571 (2012).
- Ikehara, T. & Nishi, T. Interpenetrated spherulites of poly(butylene succinate)/poly(vinylidene chloride-co-vinyl chloride) blends. An optical microscopic study. *Polym. J.* **32**, 683–687 (2000).
- Ikehara, T., Kimura, H. & Kataoka, T. Miscibility Enhancement and Formation of Interpenetrating Spherulites in Ternary Blends of Crystalline Polymers. *J. Polym. Sci. B: Polym. Phys.* **48**, 706–711 (2010).
- Qiu, Z. B., Ikehara, T. & Nishi, T. Miscibility and crystallization in crystalline/crystalline blends of poly(butylene succinate)/poly(ethylene oxide). *Polymer* **44**, 2799–2806 (2003).
- Papageorgiou, G. Z. & Bikiaris, D. N. Biodegradable poly(alkylene succinate) blends: thermal behavior and miscibility study. *J. Polym. Sci. B Polym. Phys.* **44**, 584–597 (2006).
- Jiang, N. & Abe, H. Miscibility and morphology study on crystalline/crystalline partially miscible polymer blends of 6-arm poly(L-lactide) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate). *Polymer* **60**, 260–266 (2015).
- Kuo, P. C., Chang, Y. C., Chen, C. Y. & Lo, C. T. Morphology and crystallization behavior of poly(L-lactide)/poly(butylene oxalate) blends. *J. Polym. Sci. B Polym. Phys.* **53**, 192–202 (2015).
- Di Lorenzo, M. L. Spherulite growth rates in binary polymer blends. *Prog. Polym. Sci.* **28**, 663–689 (2003).
- O'Shaughnessy, B. & Vavylonis, D. Non-equilibrium in adsorbed polymer layers. *J. Phys. Condens. Matter* **17**, R63–R99 (2005).
- Stromberg, R. R., Quasius, A. R., Toner, S. D. & Parker, M. S. Adsorption of polyesters on glass, silica, and alumina. *J. Res. Nat. Bur. Stand.* **62**, 71–77 (1959).

Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)