

Spherulite Crystallization in Poly(ethylene oxide)–Silica Nanocomposites. Retardation of Growth Rates through Reduced Molecular Mobility

Alan John WADDON^{†,††} and Zoran S. PETROVIC*

Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, U. S. A.

**Kansas Polymer Research Center, Pittsburgh State University, Pittsburgh, KS 6672, U. S. A.*

(Received July 25, 2002; Accepted October 2, 2002)

ABSTRACT: The spherulitic crystallization of nanocomposites of poly(ethylene oxide) (PEO) and silica nano-sphere filler particles was investigated using optical microscopy and differential scanning calorimetry (DSC). It was found that spherulite growth rates were retarded by the presence of the silica nano-particles. This was interpreted in terms of reduced molecular mobility caused by either geometric constraints in the confined small volumes between particles, or by an increase of the interfacial surface area at which polymer chains were pinned. There was an indication of lowering of final crystallinity and increase of amorphous content for heavily filled higher molecular weight polymer. Implications for conductivities of PEO when used as a solid electrolyte in applications such as batteries are considered.

KEY WORDS Nanocomposites / Crystallization / Poly(ethylene oxide) (PEO) / Spherulite / Mobility / Constraint / Conductivity /

In recent years well-defined particles with one or more dimensions on the scale of nanometers have been developed using various techniques. There is great interest in using such nano-particles in numerous applications, for example, optical, magnetic, electronic, and catalyst supports.^{1,2} A number of groups have used nano-particles in polymer composites in place of conventional fillers with the goals of improving properties, such as mechanical, barrier and thermal. In particular, there has been a significant level of interest in the use of clays as filler materials (*e.g.*, ref 3–9). The incorporation of such nano-sized particles into host materials offers the possibility of producing materials justifiably termed “nanocomposites”.

There are three obvious but important differences between conventionally filled polymer composites and polymer nanocomposites. First, for fillers at the nano-size scale, traditional continuum materials science in which materials properties scale with volume fraction is no longer applicable. Second, for materials filled with even moderate volume fractions of nano-sized particles, the separation between particles will also be on the scale of nanometers. In the case of polymer matrices, this may be the same size scale as the pertinent chain parameters of the host polymer such as, for instance, the r.m.s. end-to-end chain distance or radius of gyration. At high enough loadings this may be expected to eventually introduce constraints on the topology of the chain, affecting chain dynamics and properties dependent on chain dynamics. Third, the incorporation of nanometer sized particles into a matrix introduces

an enormous interfacial surface area into the system at which chain segments may be effectively pinned.

There have been a number of studies using changes in diffusion properties or crystallizability reporting decreases in chain mobility when polymers are confined within thin films. This retardation in chain dynamics has been explained primarily through increased interfacial effects.^{10–15} We have also previously observed an increase in glass transition temperature, T_g , in amorphous polyurethanes filled with nanoscopic spheres of silica.¹⁶

In the present work we focus on crystal growth rates, measured as the radial growth rate of spherulites. For this purpose we wished to use a readily crystallizable linear polymer of high crystallinity. Poly(ethylene oxide) (PEO) readily satisfies these criteria. There were two further reasons for selecting this system. First, from the point of view of potential applications, PEO is used as a solid electrolyte in batteries. It is well accepted that ionic transport in such electrolytes is through the amorphous phase. However, ionic mobilities in polymers such as PEO are limited by high crystallinities^{17–22} and therefore techniques for frustrating crystal growth and limiting crystallinity are of potential practical importance. Second, narrow molecular weight fractions of PEO were available, allowing us to remove the complications of poly-dispersity and to examine the effect of molecular weight on crystallization in such an environment. Additionally this is a material a) which has been used widely as an intercalating material in the nanocomposite community and b) in which crystalliza-

[†]To whom correspondence should be addressed (E-mail: A.Waddon@sheffield.ac.uk).

^{††}Present Address: Engineering Materials, University of Sheffield, Robert Hadfield Building, Sheffield, S1 3JD, Great Britain.

Table I. Weight fractions and corresponding estimated volume fractions of nano-silica in PEO

Wt. fraction	Vol. fraction
~ 10%	5%
~ 25%	14%
~ 50%	32%

tion in confined geometries has been examined previously.^{15, 19, 23–26}

EXPERIMENTAL

Materials

Nano-silica, having an average particle diameter of about 12 nm, was obtained from Nissan Chemical Co. as ~30 wt% dispersion in methylethylketone (MEK). The distribution of diameters ranged from 10–20 nm. Two sharp molecular weight fractions of PEOs of 86 K and 145 K g mol^{-1} with polydispersities of 1.02 and 1.03, respectively, were supplied by Toyo Soda Manufacturing, Tokyo, Japan. Approximate end-to-end distances for these polymers were 17 and 22 nm, respectively.

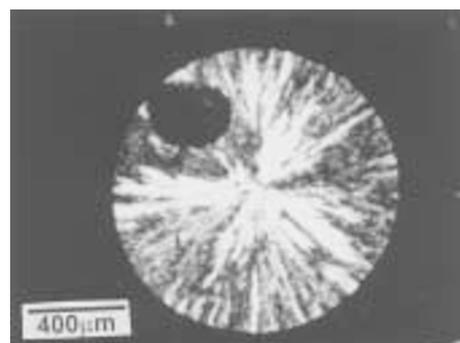
Sample Preparation

Composites were prepared by dissolving PEO in MEK at ~55 °C to form ~2 to 5% solutions and adding the required quantity of warm nano-sphere suspension to form clear solutions in the desired ratio. Solutions were cast on microscope slides at ~55 °C and the MEK evaporated to form films. Weight fractions of silica of ~10, 25, and 50% were used. At higher concentrations significant aggregation of silica was detected visually. Using approximate values of 1.0 and 2.3 g cm^{-3} for the densities of PEO and silica, respectively, the corresponding volume fractions can be estimated; these are listed in Table I. The films were melted at 100 °C to remove any residual solvent and re-crystallized on cooling.

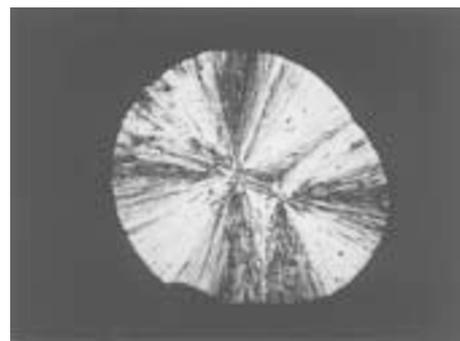
Methods of Investigation

Polarized Optical Microscopy. Films were examined with a polarizing optical microscope equipped with a Mettler Hot Stage. Samples were cooled from the melt and held at the desired isothermal crystallization temperature. Isothermal growth rates of spherulites were measured in temperature range of ~45–55 °C.

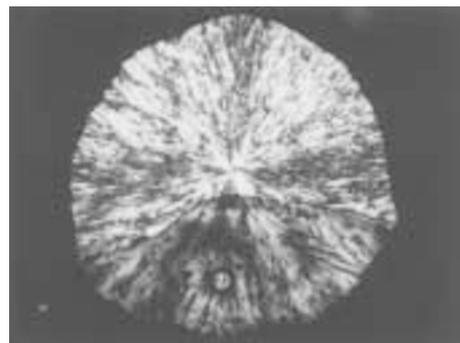
Differential Scanning Calorimetry (DSC). Melting points and heats of melting of selected materials were determined using a Thermal Analysis 2100 DSC at a heating rate of 1 °C min^{-1} . Heats of fusion of the nanocomposites were normalized for PEO content and expressed as heat per weight of PEO.



(a)



(b)

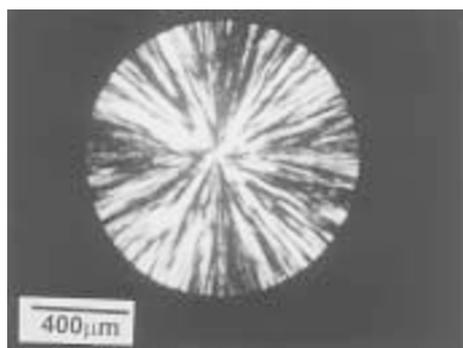


(c)

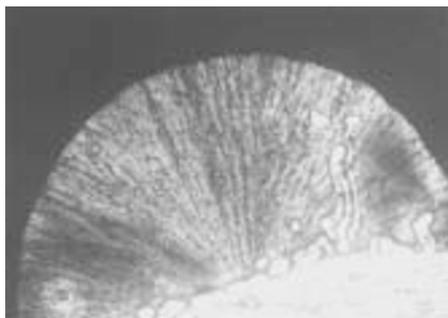
Figure 1. Spherulites of 86 K PEO filled with silica nanospheres. (a) 0%, $T_c = 53$ °C, (b) 10%, $T_c = 51$ °C, and (c) 25%, $T_c = 49$ °C. Crossed polars.

RESULTS

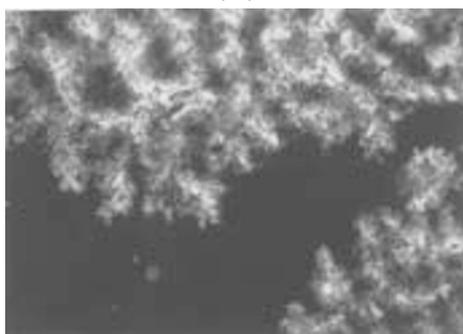
Figures 1 and 2 show examples of spherulites growing in PEO-silica nanocomposites formed with the 86 K and 145 K PEOs, respectively. Various crystallization temperatures and silica contents are shown. It was evident that spherulites became increasingly coarse in texture with increasing levels of loading. Figure 1c shows departure from a truly circular geometry for the 86 K material with 25% silica. At very high loadings there was significant increase in nucleation density and deterioration in spherulite texture. This is particularly clear in 145 K with 50% silica specimen, Figure 2c. Plots of spherulite radius against time at isothermal temperatures are shown in Figures 3 and 4 for filled samples of PEOs 86 K and 145 K, respectively. It was not possible



(a)



(b)



(c)

Figure 2. Spherulites of 145 K PEO filled with silica nano-spheres. (a) 0%, $T_c = 55^\circ\text{C}$, (b) 25%, $T_c = 47^\circ\text{C}$, and (c) 50%, $T_c = 50^\circ\text{C}$. Crossed polars.

to reliably measure the growth rate of the 145 K/50% silica material because of the especially severe disruption to the spherulite texture (Figure 2c). The traces in Figures 3 and 4 are essentially linear, consistent with a constant rate of growth at each temperature. While this may be a trivial observation for the pure, unloaded polymer, it is not necessarily obvious that this should also be the case for polymer filled with nano-particles. The positions where the plots intersect the abscissa on Figures 3 and 4 correspond to the times of growth initiation. These positions are very variable and are considered to reflect a “sporadic” rather than “instantaneous” nucleation process. In some cases the abscissae are crossed at negative values, consistent with nucleation during cooling to the isothermal temperature.

Growth rates were calculated from the slopes of lines in Figures 3 and 4 and are plotted as functions of tem-

Table II. 145 K PEO nano-composite. Melting points and heats of melting (heats of fusion expressed per gram of PEO)

Silica content/wt%	Melting point/ $^\circ\text{C}$	Heat of fusion/ J g^{-1}
0	63.6	118
10	61.8	111
25	61.5	96
50	59.4	85

perature in Figures 5 and 6 for PEOs of 86 K and 145 K molecular weights, respectively. Importantly, for present purposes, it is clear that growth rates decreased significantly with volume fraction of silica. In general, growth rates also increased with increasing under-cooling (decreasing temperature). However, it is noted that the recorded growth rate for the higher molecular weight PEO with the highest loading showed a maximum and then a decrease with increasing under-cooling (Figure 6).

Table II shows the melting points and heats of fusion for the samples prepared with 145 K PEO. It is apparent that there was a lowering of the heat of fusion with silica content, indicating lower values of crystallinity. The melting points, however, were only slightly affected.

DISCUSSION

Polymers usually crystallize from the isotropic melt as spherulites. This form of crystallization is characterized by radial growth of crystals from a central nucleus. In polymers each individual crystal is a chain-folded lamella of thickness $\sim 10\text{--}30$ nm in which chains lie tangential to the spherulite. The kinetics of spherulitic growth at constant temperature are characterized by a constant rate of growth up until near the point where neighboring spherulites impinge. The uncrystallizable species in the material are rejected from the developing crystal, as shown in the classical work of Keith and Padden (*e.g.*, ref 27). These can segregate to either a) the lamellar surfaces within the spherulite, or b) to the circumferential boundary between spherulites. In the present case one point of interest is how the presence of nano-spheres, which can be considered as non-crystallizable “impurities”, affect the kinetics of the growth process. Our results clearly show that the presence of silica significantly lowers growth rates. This is consistent with a retardation of chain mobility. A second point of interest is how the nano-spheres, which, of course, are different from the non-crystallizable components of the polymer itself, are accommodated morphologically. In one extreme case particles may be rejected to spherulite borders, causing an increase in nano-filler concentration in the uncrystallized melt and,

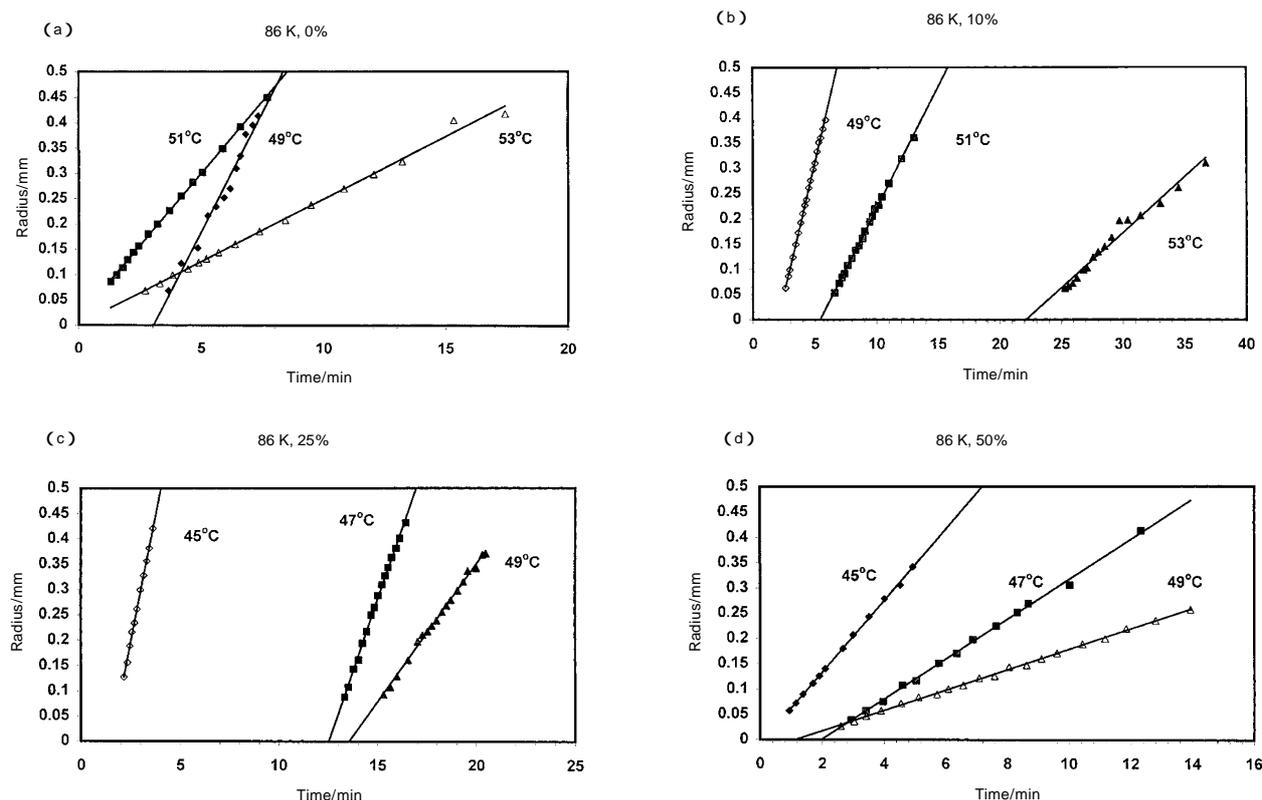


Figure 3. Spherulite radius plotted against time for 86 K PEO nanocomposites Wt% of silica: (a) 0%, (b) 10%, (c) 25%, and (d) 50%.

consequently, a gradual decrease in growth rate during crystallization. In the other extreme, particles may be incorporated entirely into the body of the spherulite in the same concentration as in the melt, in which case there will be no change in concentration during crystallization and therefore no change in growth rate. In the present case it is evident that growth rates remained essentially constant with time and that they fell with increasing silica content over the range of conditions used. This therefore implies that the concentration of silica in the uncrystallized melt ahead of the growth front did not change throughout growth and that silica particles were accommodated within the body of the spherulite rather than segregating to the boundaries.

The above conclusion leads to consideration of how the silica nano-particles are accommodated within the spherulite. At ~ 12 nm diameter, the nano-particles are enormous compared to the cross-sectional area occupied by the PEO chain in the crystal lattice which is calculated to be 0.214 nm^2 (from data in ref 28). Inclusion of such particles within the crystal is clearly impossible. Also, such inclusion would cause appreciable disruption of the crystal lattice and consequent suppression of melting points, which was not observed. However, the reduction in the heat of fusion of PEO with increasing nano-particle concentration observed with 145 K g mol^{-1} PEO, indicates a decrease in the fraction

of PEO able to crystallize.

The reduction in growth rates may result from the two factors introduced earlier. First, purely geometric, spatial constraints on chains may be introduced by confining them in the restricted space between particles. This may frustrate their mobility and ability to attach to a growing crystal face. Second, chains may be effectively pinned at surfaces (external or internal), thereby providing fixed contact points, which restrict molecular motion. Such interfacial effects have been proposed on the basis of diffusivity studies^{10, 14} and crystallization studies^{11–13, 15} and the literature suggests that pinning at interfaces is more likely than purely spatial confinement. There is no doubt that in our system the silica nano-spheres provide an enormous internal interfacial area, which, if the latter mechanism is effective, would provide a ready explanation for the reduction in growth rates. We also recognize that silica has a tendency to absorb OH groups on the surface which may provide a means of hydrogen bonding with the oxygen in PEO, hence providing a mechanism for such interfacial pinning. It is also noted that such pinning of chains at particles would prevent large scale segregation of particles to spherulite boundaries, consistent with our observations of constant rate of advance of the crystal growth front and inference that nano-particles are accommodated within the spherulite. However, at this stage, in

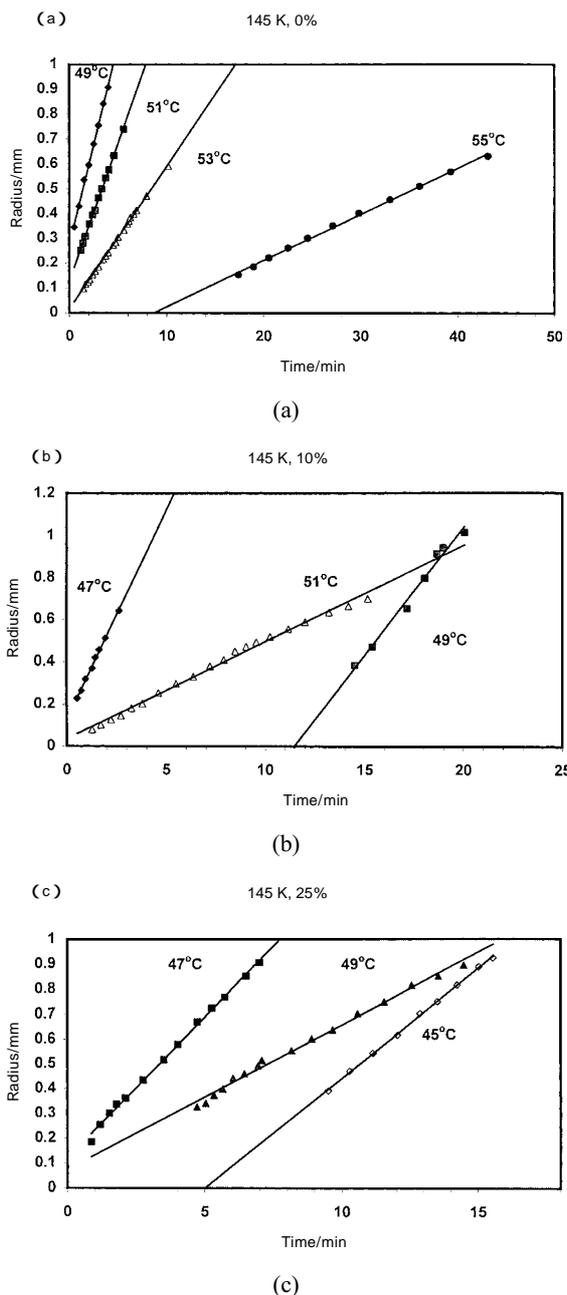


Figure 4. Spherulite radius plotted against time for 145 K PEO nanocomposites Wt% of silica: (a) 0%, (b) 10%, and (c) 25%.

the absence of supplementary information, the relative contributions to the reduction in growth rates from spatial confinement of the polymer into small volumes between nano-spheres or from interfacial pinning, cannot be unambiguously separated.

The observation of the maximum in growth rates with decreasing temperature in the higher molecular weight sample with highest amount of loading is reminiscent of the behavior of high T_g , slowly crystallizing, semi-flexible polymers, such as PET or PEEK. The appearance of this maximum is consistent with the notion that the presence of nano-spheres limits the ability of chains to move. It is also evident that the final degree of crystallinity of PEO can be reduced in the

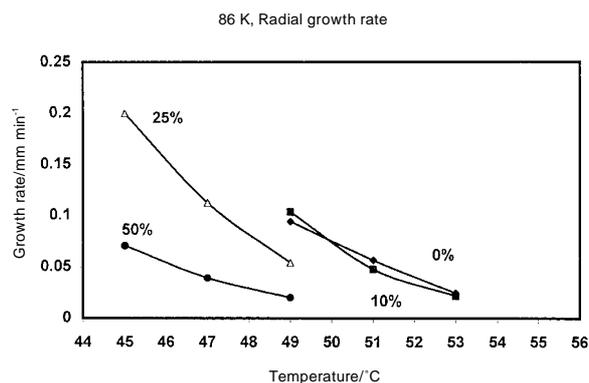


Figure 5. Isothermal radial growth rates plotted against temperature of crystallization for nanocomposites with 86 K PEO.

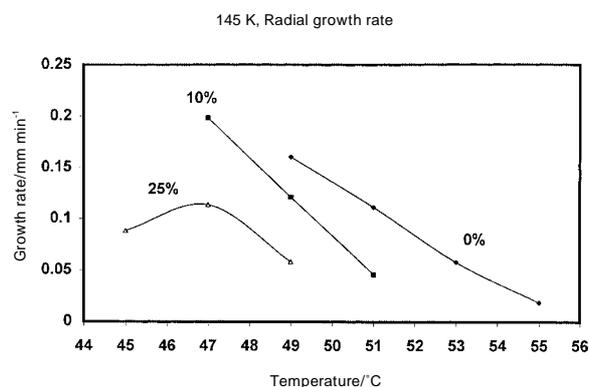


Figure 6. Isothermal radial growth rates plotted against temperature of crystallization for nanocomposites with 145 K PEO.

case of the higher molecular weight polymer. Similarly, Rabolt and co-workers¹³ also found that, as well as reducing growth rates, final degrees of crystallinity could be lowered in ultra-thin spin coated films of crystallizable polymers.

For the specific case of PEO in battery applications, it has previously been shown that crystallinities in PEO-Li electrolytes can be reduced by the addition of micron sized inorganic particles. Furthermore, this simultaneously increased conductivity and mechanical properties.¹⁹ The reduction in crystallinity was considered to be responsible for the associated increase in conductivity. It is expected that the introduction of nano-scale particles would be more efficient than micron-scale counterparts in these respects, suggesting that nano-particles may inhibit PEO crystallization and improve mechanical properties with minimum dilution effect of filler content. This may possibly lead to improved performance of PEO based solid electrolytes.

CONCLUSIONS

It has been shown that growth rates of spherulites in nanocomposites of PEO filled with silica nano-spheres of diameter ~ 12 nm are progressively retarded as nano-

particle content increases. This reduction in growth rate is attributed to a reduction in chain mobility caused by the nano-spheres. The mechanism by which molecular mobility is reduced may be spatial confinement of chains in the small volumes between nano-particles. It is reasonable that, at high enough volume fractions in a well-dispersed system, the size of inter particle distances will be on the approximate size scale as molecular parameters such as radius of gyration and may therefore constrain chain topology. However, there is considerable support from the literature for a second mechanism of preferential location and effective “pinning” of chains at the silica-polymer interface which, for filler particles on the nano-size scale, is clearly enormous, and this mechanism is considered more probable. A reduction in crystallinity for the higher molecular weight PEO with the highest loading of silica was also observed.

Acknowledgment. The support of the NSF funded MRSEC at the University of Massachusetts, Amherst is acknowledged.

REFERENCES

1. D. Y. Godovsky, *Adv. Poly. Sci.*, **153**, 163 (2000).
2. C. J. Hawker, J. L. Hedrick, R. D. Miller, and W. Volksen, *MRS Bull.*, **25**, 54 (2000).
3. G. Lagaly, *Appl. Clay Sci.*, **15**, 1 (1999).
4. P. B. Messersmith and E. P. Giannelis, *Chem. Mater.*, **6**, 1719 (1994).
5. R. A. Vaia, K. D. Jandt, E. J. Kramer, and E. P. Giannelis, *Macromolecules*, **28**, 8080 (1995).
6. A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, and O. Kamigaito, *J. Mater. Res.*, **8**, 1179 (1993).
7. P. C. LeBaron, Z. Wang, and T. J. Pinnavaia, *Appl. Clay Sci.*, **15**, 11 (1999).
8. R. Krishnamoorti, R. A. Vaia, and E. P. Giannelis, *Chem. Mater.*, **8**, 1728 (1996).
9. A. S. Zerda and A. Lesser, *J. Polym. Sci., Polym. Phys. Ed.*, **39**, 1137 (2001).
10. B. Frank, A. P. Gast, T. P. Russell, H. R. Brown, and C. Hawker, *Macromolecules*, **29**, 6531 (1996).
11. C. W. Frank, V. Rao, M. M. Despotopoulou, R. F. W. Pease, W. D. Hinsberg, R. D. Miller, and J. F. Rabolt, *Science*, **273**, 912 (1996).
12. G. Reiter and J. Sommer, *Phys. Rev. Lett.*, **80**, 3771 (1998).
13. M. M. Despotopoulou, C. W. Frank, R. D. Miller, and J. F. Rabolt, *Macromolecules*, **29**, 5797 (1996).
14. X. Zheng, B. B. Sauver, J. G. van Alsten, S. A. Schwarz, M. H. Rafailovich, J. Sokolov, and M. Rubinstein, *Phys. Rev. Lett.*, **74**, 407 (1995).
15. K. Dalnoki-Veress, J. A. Forrest, M. V. Massa, A. Pratt, and A. Williams, *J. Polym. Sci., Polym. Phys. Ed.*, **39**, 2615 (2001).
16. Z. S. Petrovic, I. Javni, A. J. Waddon, and G. Banhegyi, *J. Appl. Polym. Sci.*, **76**, 133 (2000).
17. J. R. MacCallum and C. A. Vincent, Ed., in “Polymer Electrolyte Review”, Elsevier Applied Science, London, 1987.
18. J. Li, E. A. Mintz, and I. M. Khan, *Chem. Mater.*, **4**, 1131 (1992).
19. F. Croce, B. Scrosati, and G. Mariotto, *Chem. Mater.*, **4**, 1134 (1992).
20. K. M. Abraham, Z. Jiang, and B. Carroll, *Chem. Mater.*, **9**, 1978 (1997).
21. L. M. Bronstein, C. Joo, R. Karlinsey, A. Ryder, and J. W. Zwanziger, *Chem. Mater.*, **13**, 3678 (2001).
22. R. Tanaka, M. Sakurai, H. Sekiguchi, H. Mori, T. Murayama, and T. Ooyama, *Electrochim. Acta*, **46**, 1709 (2001).
23. Y. H. Hyun, S. T. Lim, H. J. Choi, and M. S. Jhon, *Macromolecules*, **34**, 8084 (2001).
24. J. Kwiatkowski and A. K. Whittaker, *J. Polym. Sci., Polym. Phys. Ed.*, **39**, 1678 (2001).
25. J. Bujdak, E. Hackett, and E. P. Giannelis, *Chem. Mater.*, **12**, 2168 (2000).
26. S. C. Jiang, C. D. Qiao, S. Z. Tian, X. L. Ji, L. J. An, and B. Z. Jiang, *Polymer*, **42**, 5755 (2001).
27. H. D. Keith and F. J. Padden, *J. Appl. Phys.*, **35**, 1270 (1964).
28. F. P. Price and R. W. Kilb, *J. Polym. Sci.*, **57**, 395 (1962).