

Liquid-Induced Crystallization of Poly(Ethylene-2,6-Naphthalate)

Previous studies devoted to the liquid-induced crystallization of polymers have primarily focused on poly(ethylene terephthalate) (PET). Thorough summaries of the morphology induced in PET by this type of crystallization exist in the literature.¹⁻³ Recent work has also focused on the fundamental aspects of liquid induced crystallization.^{4,5} Some limited studies concerning the liquid-induced crystallization of initially amorphous poly(ethylene-2,6-naphthalate) (PEN) have indicated that this polymer can also readily be crystallized in certain liquids such as dioxane and methylene chloride, resulting in a particularly distinct spherulitic texture.³ In the present study, similar effects have been noted, along with observations concerning the time and temperature dependence of the formation of this spherulitic texture induced by dioxane and aniline liquid.

In the dioxane-PEN case, immersions at 24°C seem to result in the formation of distinct clusters of small spherulites (on the order of 1 to 2 μm in diameter) on the film surface, clusters which appear to increase in number with increasing immersion time [see representative scanning electron micrograph (SEM) in Fig. 1]. With increasing immersion temperature, these spherulitic clusters seem to become more evenly dispersed over the entire film surface until approximately 50°C, at which temperature the sample appears to be uniformly covered with spherulitic material and cavitation is in evidence. The size of the spherulites themselves, however, apparently does not vary strongly with either immersion time or temperature. Polarized optical microscopy (OM) studies of these dioxane-treated materials show distinct maltese cross patterns, indicative of optically anisotropic spherulites.

Treatments of PEN in aniline liquid appear to result in distinct spherulitic structure rather uniformly dispersed over the entire sample surface at 24°C. Surface cavitation is also quite prevalent at this temperature. While amines are known to degrade polyesters, the degradation process requires a much longer time scale than was typically used in this study for the immersions of PEN in aniline.⁶ Increasing the immersion temperature (up to 75°C in our studies) has no significant effect on the spherulite size, but does seem to increase the uniformity of the surface cavitation. There does not appear to be any significant difference in the spherulite sizes produced by either dioxane or aniline in PEN. Figure 2 shows a representative SEM of the typical morphology induced in PEN by aniline. Also displayed in this figure is an SEM of a fracture surface of a PEN film immersed in aniline, demonstrating that this spherulitic structure extends into the bulk of the film as well. OM studies of these aniline-treated PEN films again verify that these materials have characteristic optically anisotropic spherulitic texture.

Fracture surfaces of PEN immersed in dioxane liquid at 24°C reveal an apparent front of liquid penetrating the polymer. For the PEN-dioxane system at 50°C, a distinct permanent void is left

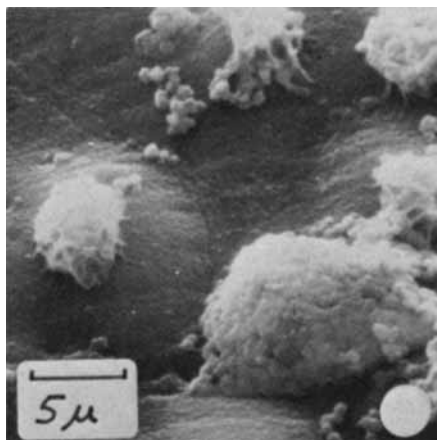


Fig. 1. Representative SEM of the surface of an initially amorphous PEN film immersed in dioxane liquid 90 min at 24°C.

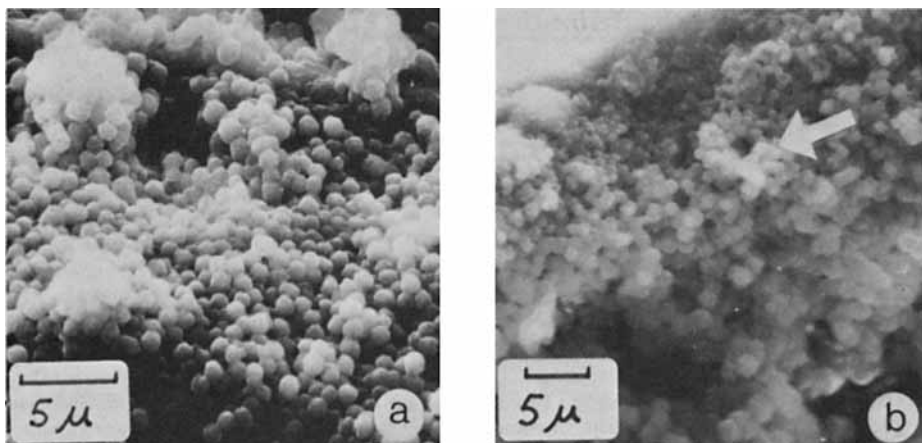


Fig. 2. (a) Representative SEM of the surface of an initially amorphous PEN film immersed in aniline liquid 4 hr at 24°C. (b) Representative SEM of the fracture surface of an initially amorphous PEN film immersed in aniline liquid one hr at 50°C. Arrow indicates fractured surface which itself is slightly tilted in the SEM stage, thus slightly distorting the relative spherulite sizes (all spherulites in fracture surface approximately equal in size).

at the film center following complete penetration by the liquid. Furthermore, examination of fracture surfaces of this system also reveals that a distinct spherulitic texture is evident throughout the entire film cross section for the 50°C immersions. Figure 3 shows a representative SEM of this behavior.

Based on these limited studies of PEN, some comparisons can be made between the morphologies induced in PEN and PET resulting from crystallization by liquids. Specifically, spherulitic texture appears to be induced in both polymers as a result of this type of crystallization, and in both cases the characteristic spherulite sizes do not seem to be strongly dependent on either the crystallization temperature or the liquid type. Wide-angle x-ray scattering patterns of PEN crystallized in both dioxane and aniline show rather intense reflections that are in general much broader than those observed in PEN thermally crystallized at temperatures only 20° higher than its glass transition. Similar results have been noted for liquid-induced crystallized PET, and have been attributed to rather small-sized yet profuse crystallites induced by the liquid treatments.¹

On the other hand, PEN shows a very high degree of internal cavitation when crystallized in aniline at all the temperatures investigated and in dioxane at and above 50°C. This internal cavitation is so pronounced that fracture surfaces of these materials reveal distinct spherulitic structure throughout the entire film cross section, as noted via SEM. PET only shows a cavitated surface

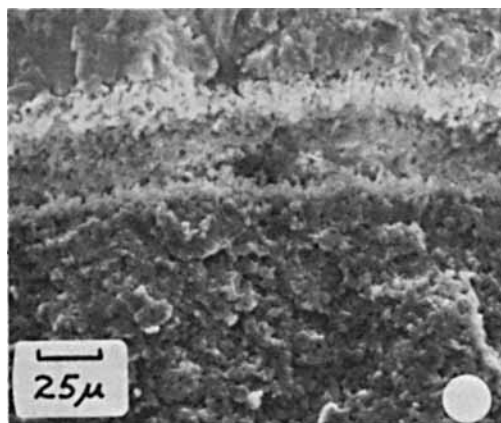


Fig. 3. Representative SEM of the fracture surface of an initially amorphous PEN film immersed in dioxane liquid 10 min at 50°C. Arrow indicates central void.

layer when crystallized in such liquids as methylene chloride and dioxane, and the cavitated layer only extends a short distance into the film's interior. Thus, this behavior in PEN directly demonstrates that spherulitic texture is induced throughout films undergoing liquid-induced crystallization, an effect strongly implied but not evidenced as dramatically in PET.^{6,8}

It can also be noted that complete penetration of PEN by dioxane liquid at 50°C causes a large, permanent void at the film center, while no such void has been noted in our previous investigations of completely liquid-penetrated PET.^{7,9} Small-angle x-ray scattering studies of PEN liquid-induced crystallized in either aniline or dioxane show only diffuse scattering with no discernible intensity maxima. The previously mentioned extensive voids in this material probably lead to this behavior.

References

1. L. Rebenfeld, P. J. Makarewicz, H.-D. Weigmann, and G. L. Wilkes, *J. Macromol. Sci., Rev. Macromol. Chem.*, **15**, 279 (1976).
2. E. L. Lawton, *Text. Chem. Color*, **5**, 27 (1973).
3. A. B. Desai and G. L. Wilkes, *J. Polym. Sci. Symp.*, No. **46**, 291 (1974).
4. P. J. Makarewicz and G. L. Wilkes, *Am. Chem. Soc. Polym. Prepr.*, **18**(2), 360 (1977).
5. P. J. Makarewicz and G. L. Wilkes, *Am. Chem. Soc. Polym. Prepr.*, **18**(2), 366 (1977).
6. C. Chu and G. L. Wilkes, *J. Macromol. Sci., Rev. Macromol. Phys.*, **10**, 551 (1974).
7. P. J. Makarewicz, Ph.D. Thesis, Department of Chemical Engineering, Princeton University, 1977.
8. H. G. Zachmann, *Faser. Text.*, **18**, 95 (1967).
9. P. J. Makarewicz and G. L. Wilkes, submitted to *J. Appl. Polym. Sci.*

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