

Influence of the Crosslinking on the Crystallization of Poly(tetramethylene terephthalate)

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ABSTRACT: Isothermal crystallization of linear and crosslinked PTT has been studied in order to find the influence of crosslinking on the mechanism of crystallization. The samples were crystallized from the melt in the temperature range from 90 to 200°C and they were studied by roentgenographic, microscopic, and light scattering methods. It was found that the crosslinking does not change the structure of PTT crystallites. However, the influence on the type of spherulites formed is significant. In the linear polymer, depending on the crystallization temperature, spherulites of 0-90 (untwisted lamellae) and 45 (lamellae twisted at $\alpha \cong 45^\circ$) types of optical axis orientation were formed, while in the crosslinked system, only spherulites of 0-90 type were observed. This was explained to be a result of the presence of junctions, which make the twisting of the lamellae impossible.

KEY WORDS Poly(tetramethylene terephthalate) / Crosslinking / Crystallization / Morphology /

In the recent studies^{1,2} on the crystallization of poly(tetramethylene terephthalate) (PTT) it was found that, depending on the crystallization temperature, this polymer forms spherulites of either 0-90 or 45 type of the optical axes¹ orientation. The PTT samples crystallized from the melt at temperatures above 180°C gave the first type (0-90), while the samples crystallized in the range of 0-180°C gave the second type (45) of spherulites.

The formation of a given type of spherulites is explained³⁻⁶ by the helical growth of fibrils with the particular angle between a tangent to the helix and the tangent to the circular cross section of the cylinder on which the helix is imagined to be wound. When the helical angle $\alpha \cong 90^\circ$ (the helix is very elongated) the principal axis of polarizability is parallel to the radius and the spherulites of 0-90 type, which give the scattering pattern H_V of 45° type, are formed. When the helical angle $\alpha \cong 45^\circ$ and the helix pitch is smaller than the spherulite radius, the principal axis of polarizability is twisted at the same angle and the spherulites of 45 type are formed (H_V scattering pattern of 0-90 type).

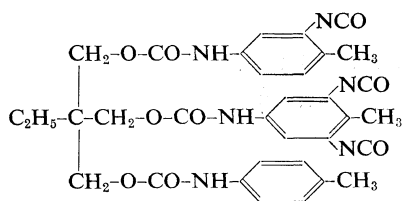
The helical growth of the lamellae is conditioned by their undisturbed twisting. This twist-

ing can be difficult or even impossible in the crosslinked system. So the crosslinking ought to have significant influence not only on the kinetics of crystallization,⁷⁻⁹ but also on the morphology. This problem has been studied in this paper on the basis of linear and crosslinked PTT.

EXPERIMENTAL PROCEDURES

Sample Preparation

PTT with -OH terminal groups has been used for the studies. Due to this group the crosslinking by the reaction with triisocyanate was possible. The suitable polymer was obtained by the glycolysis of the high molecular polymer (mp 221—223°C) with 1,4-butanediol. The reaction was carried out in the melt at 225°C using 10 wt% of glycol.¹⁰ As a result PTT with a mp of 202—205°C and a molecular weight of 960, determined by the cryoscopic method, was obtained. The IR analysis showed the strong absorption band of the -OH groups (3400—3600 cm^{-1}) and the NMR spectrum did not point out the existence of the -CH₃ end groups. The obtained polymer reacted with the triisocyanate of the formula:



The reaction was carried out in dimethylformamide at 153°C (bp of the solvent) during 1 hr, and as a result the insoluble crosslinked polyurethane (PU) was obtained.

Crystallization Studies

The isothermal crystallization from the melt of linear PTT and crosslinked PU was studied. The samples were prepared by melting a small amount of polymer between the microscope cover glasses. After melting, the samples were heated up to 215°C, maintained for 10 min at this temperature and then transferred into the crystallization bath containing silicone oil. Temperatures of the crystallization bath were chosen in the range from 90 to 200°C at every 10°C. The lower temperatures were not applied because at 80°C even 20 hr of heating did not cause the crystallization of the crosslinked polymer. The crystallization times depended on the rate of the process at given temperatures. The samples were crystallized isothermally until the crystallized structures were seen under the polarizing microscope. The crystallization rate of crosslinked polymer was much smaller than in the case of linear polymer, as was found previously.⁷⁻⁹ Characterization of the samples was done by: (1) roentgenographic method using diffractometer URS-IM, radiation NiK_α, (2) optical microscopy using MPI-5 polarizing microscope, and (3) small-angle light scattering using He-Ne laser as a light source.

RESULTS

The results of the roentgenographic studies are shown in Figure 1. The curves represent the crystalline structures of linear (curve 1) and crosslinked (curve 2) polymers. Both curves are qualitatively the same. This indicates that both polyester and polyurethane crystallize in the same crystal system. It means that in the polyurethane

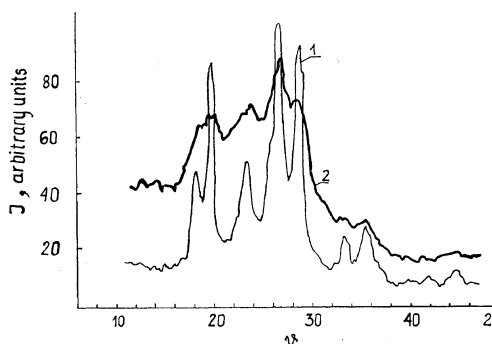


Figure 1. X-ray diffraction curves of linear (1) and crosslinked (2) PTT.

only polyester segments between junctions crystallize. The presence of junctions does not influence the structure of the polyester unit cell. Therefore, crystallization of the crosslinked polyurethane can be treated as the crystallization of the polyester itself, and the observed changes in the structure can be explained as a result of the crosslinking of the system. Microscopic observations showed that at all temperatures studied the samples possessed spherulitic morphology. The type of the spherulites was determined by the small-angle light scattering method (Table I). In the samples of the starting polyester two types of spherulites, *i.e.*, 0-90 (Figure 2) and 45 (Figure 3) were obtained, depending on the crystallization temperature. This is in agreement with the results published by Misra and Stein¹. In the range of 160–200°C only the spherulites of 0-90 type were observed, while in the range of 100–140°C solely the spherulites of 45 type were formed, but at the temperatures of 90, 150, and 160°C both types of spherulites occurred. In the crosslinked samples only spherulites of 0-90 type were observed, independently of the crystallization temperature.

Table I. Determination of the type of the spherulite by the small-angle light-scattering method.

Type of spherulites	Temperature of crystallization, °C	
	PTT	PU
0-90	90 150–200	90–200
45	90–160	—

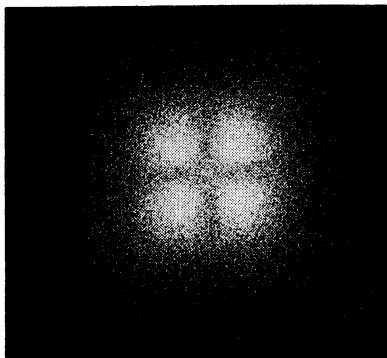


Figure 2. H_v scattering pattern of PTT spherulites of 0-90 type of optical axes orientation.

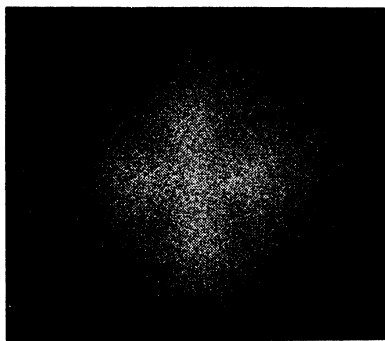


Figure 3. H_v scattering pattern of PTT spherulites of 45 type of optical axes orientation.

CONCLUSIONS

The experimental results presented above show that crosslinking of PTT does not change the manner of primary structure (crystallites) formation. So, the crystallization of crosslinked polymer can be considered as a crystallization of the linear polyester on which the presence of junctions has a pronounced effect. The presence of junctions reduce the crystallization rate of PTT, but the quantitative effect has not been deter-

mined yet. It was found, however, that the crosslinking has a significant influence on the mechanism of the formation of PTT spherulites. In the crosslinking system, only spherulites of 0-90 type were found, while in the linear PTT, depending on the crystallization temperatures, two types, 0-90 and 45, arose. This can be explained by taking into account the crosslinking which makes the twisting of the lamellae impossible. As a result, only spherulites of 0-90 type with untwisted lamellae could be formed.

These results confirmed experimentally the theory of the spherulite growth mechanism.^{3,11} This mechanism (helical growth of radially oriented lamellae) was proposed mainly on the basis of the polarizing and electron microscope studies.

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