Properties of Semicrystalline Polyolefins.   IV. Crystallization Phenomena in Poly-3-Methyl-1-Butene

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Synopsis

A study has been carried out of the physical and mechanical properties and crystallization behavior of poly-3-methyl-1-butene (poly-3-MB).   The melt behavior of poly-3-MB was examined by means of the depolarized light intensity (DLI) technique. These birefringence studies indicated the onset of motion in the crystalline phase of poly-3-MB at about 100°C. (over 200°C. below the melting point).   These studies also showed that limited molecular motion may occur at room temperature, i.e., about 25°C. below the glass transition temperature of poly-3-MB.

Poly-3-methyl-1-butene (poly-3-MB) is an extremely high-melting polyolefin.[1,2]   Its high melting point and associated high glass transition temperature are a reflection of polymer rigidity, which in turn is reflected in the physical and mechanical properties of the polymer.   Very little, however, has been reported on the morphology of this very interesting polymer and the effect of temperature on its properties.

In studying the development of crystallinity and spherulites in polymers, measurements have been made of changes in density, specific volume, or intensity of crystallinity bands in the infrared.   Direct observation of the size, number, and rate of growth of spherulites has also been employed. A technique that has special advantages is one which involves a measurement of the increase or decrease in depolarization of plane-polarized light of a crystallizing or melting polymer sample.   Magill's work[3,4] has shown that the rate of depolarization of light by a polymer sample crystallizing under essentially isothermal conditions parallels the development of crystallinity.   The depolarized light intensity (DLI) technique has been used in the study of isotactic polypropylene,[4–6] nylon 66,[7] nylon 6,[8] and poly-4-methyl-1-pentene.[9]

EXPERIMENTAL

Preparation of Poly-3-MB

All polymerizations were performed in a dry, oxygen-free nitrogen atmosphere.   The reactions were carried out in a stirred, stainless steel,

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pressure autoclave which was assembled while hot and purged with a stream of dry nitrogen. The 3-methyl-1-butene (3-MB) monomer was distilled through a column containing anhydrous barium oxide and calcium sulfate. Hydrocarbon diluents were percolated through activated alumina and stored over freshly cut sodium ribbon. The dry 3-MB monomer and hydrocarbon diluent were added to the cooled reactor followed by the catalyst slurry consisting of an alkyl aluminum and a transition metal halide. The polymerization was carried out at 100°C. and 60 psig for 2 hr. The reactor contents were cooled and the catalyst deactivated by the addition of acetyl acetone and isopropyl alcohol. The polymer was precipitated with 2 liters of isopropyl alcohol. After filtration and washing with alcohol, the polymer was stabilized and dried *in vacuo* for 16 hr. at 40°C. The test methods are described in previous publications.[10]

Melt Behavior Studies

The melt behavior of poly-3-MB was examined by using a polarizing microscope equipped with a hot stage, photomultiplier tube, and an $X-Y$ recorder.[9] Plots of light intensity versus temperature were obtained. The light transmitted through the sample placed between crossed Nicol prisms is assumed to be a function of the birefringence resulting from the crystallinity of the polymer. The film samples for these studies were prepared by compression molding at elevated temperatures followed by rapid cooling.

Dynamic Mechanical Properties

A Zwick torsional damping tester, Model Z466 (Zwick und Co. KG, Einsingen bei Ulm-Donau, West Germany) was used for measuring the shear modulus and mechanical damping of the polymers. The tester was modified for investigating torsional elasticity and damping effects in rigid plastics. The frequency range of the instrument is about 0.1–10 cycle/sec. One end of the specimen is rigidly clamped while the other end is fixed to a firmly supported disk of a known moment of inertia. The disk bears a small mirror, and the torsional oscillations are recorded on a photo-potentiometer by means of a light beam reflected from the mirror. The output is fed to an oscilliscope where the damped sine wave generated by the sample is recorded by a Polaroid camera.

RESULTS AND DISCUSSION

Properties of Poly-3-MB

The poly-3-MB used in these experiments was shown by x-ray diffraction to be highly crystalline. This polymer was a brittle material having the properties shown in Table I.

Poly-3-MB normally crystallizes without large spherulite growth when observed under the polarizing microscope. Typical is the photomicrograph

TABLE I.
Properties of Poly-3-MB

Property	
Crystalline melting point, °C.	305 ± 5
Tensile at break, psi	5000
Elongation at break, %	3
Flexural modulus, psi	490,000
Flexural yield strength, psi	6900
Izod impact at 25°C., ft.-lb./in.	
Notched	0.3
Unnotched	1.4
Heptane-insolubles, %	96
Heat distortion temperature, °C.	>185

shown in Figure 1.   However, on slow cooling, larger and under some cir-
cumstances more well defined spherulites are formed, as shown in Figure 2.
It is apparent that as the poly-3-MB crystallized from the melt, fracture
had occurred not only at spherulite boundaries but also throughout the
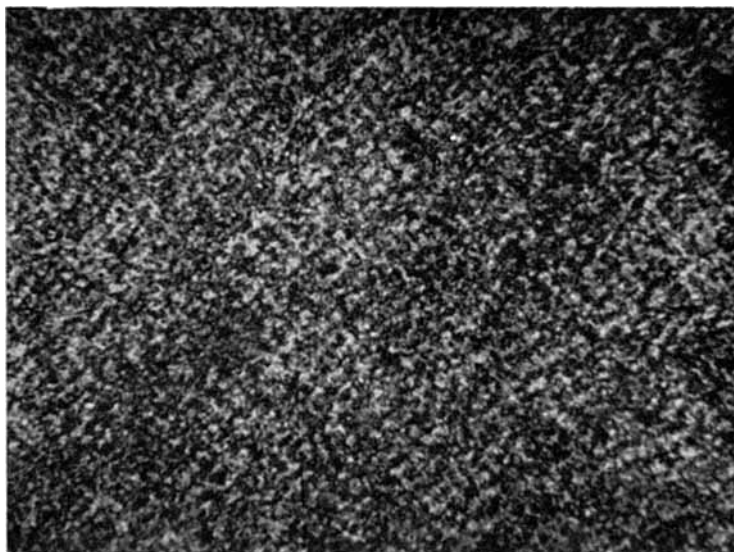spherulites.   This is the result of considerable contraction during the

Fig. 1. Photomicrograph of compression-molded film of poly-3-MB.

crystallization process and insufficient internal mobility to accommodate
the stresses generated by the contractions.   This tendency to marked
spherulitic fracture could contribute significantly to the very poor impact
properties observed with many samples of poly-3-MB.   At ambient tem-
peratures, poly-3-MB is well below its T_g,[11] and the stress–strain curves
show brittle fracture.   The onset of yield characteristics was observed at
about 100°C.   The significance of this is discussed below.

Fig. 2. Photomicrograph of poly-3-MB film after melting and slow cooling.

When poly-3-MB is compression-molded it exhibits ~5% mold shrinkage. The magnitude of this volume change suggests that the molecular orientation present in the solid cannot extend over large distances in the liquid phase. However, the rapid formation of spherulites in these ex-
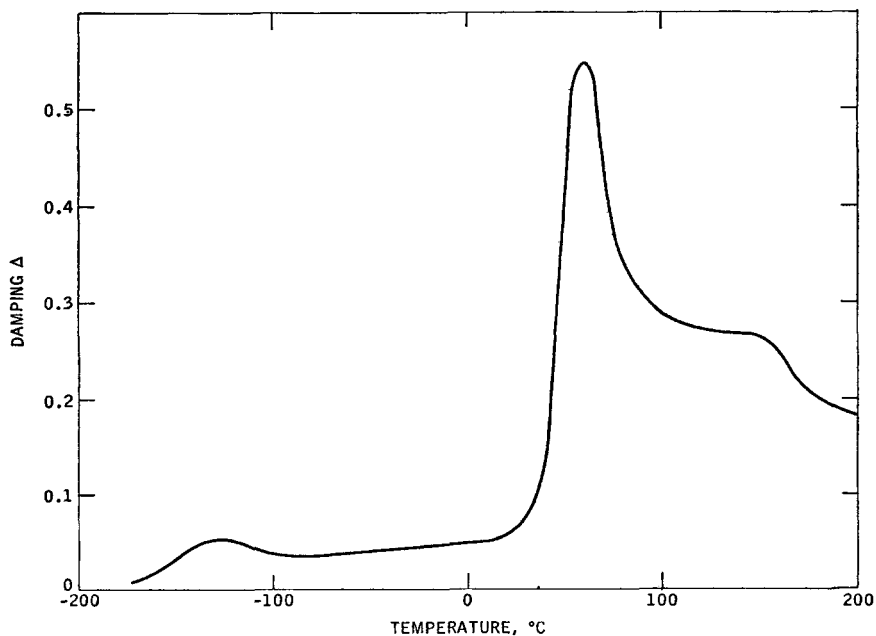

Fig. 3. Composite damping curve.

periments probably stems from suitable short-range molecular orientation or order in the melt.   Such order may have its origin not only in molecular chain folding but also in chain alignment present in the melt.

Transitions

The dynamic mechanical properties of poly-3-MB were studied in the temperature range of -190 to $+90°C$. by Woodward et al.[12] and in the temperature range of 20–200°C. in our laboratories.[13]   The combined data are shown in Figure 3 as a damping versus temperature curve.   There is a low temperature damping peak at about $-120°C$., a damping peak associated with the glass transition at about 60°C., and a high-temperature process starting at about 100°C. and extending to about 150 or 160°C. This latter relaxation appears to be related to the onset of crystal disorder in the crystalline phase.   This onset of motion in the crystalline phase is also evident in the birefringence–temperature (DLI) curve of poly-3-MB.

Depolarized Light Intensity (DLI) Data

The DLI–temperature curve for poly-3-MB is shown in Figure 4.   It differs markedly from the DLI curves of other semicrystalline polyolefins studied.   This can be seen by comparison of Figure 4 with the curves in Figure 5 for poly-4-methyl-1-pentene and polyethylene.   DLI curves of polypropylene, polybutene-1, and nylon resemble in shape the curve obtained for polyethylene.   Although no correction has been made for scattering, such a correction does not change the shapes of the DLI curves under discussion.
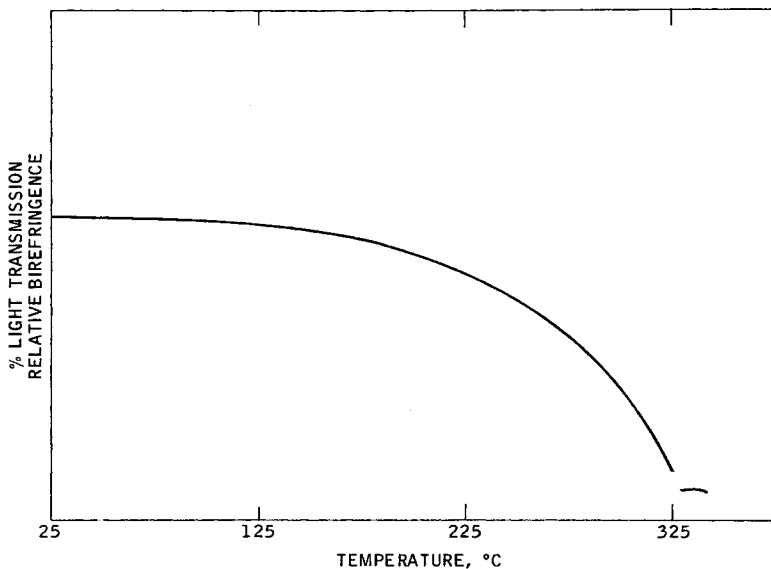

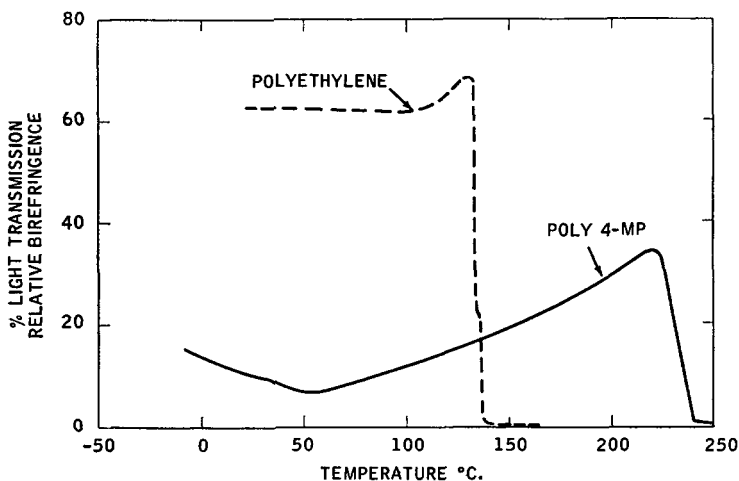Fig. 4. DLI curve for poly-3-MB.

Fig. 5. DLI curves for polyolefins.

The DLI data in Figure 4 were obtained on compression-molded film that had been aged at least 24 hr. There are several factors that could influence the shape of the poly-3-MB curve; namely (1) the effect of temperature *per se* on the birefringence (or index of refraction) of poly-3-MB or (2) the adverse effect of temperature on the crystallinity of poly-3-MB. Although the first was observed for poly-4-methyl-1-pentene,[9] it does not appear to be the phenomenon occurring here. It is the onset of motion in the crystalline phase that appears to determine the shape of the poly-3-MB curve. This conclusion is based upon the damping–temperature data in Figure 3 and on a comparison of the DLI versus temperature data with the x-ray crystallinity versus temperature data of Natta et al.[14] In Figure 6, the poly-3-MB data of Figure 4 have been replotted as per cent retention of room temperature (25°C.) crystallinity versus temperature. The conversion from per cent light transmission to per cent retention of crystallinity was made with the assumption that:

$$\% \text{ crystallinity retention} = (I_0 - I)/(I_0 - I_f)$$

where I_0, I_f, and I are the initial DLI reading, final reading after melting, and the DLI reading at a given temperature, respectively. The broken line represents Natta's x-ray data on the effect of temperature on crystallinity. The agreement is surprisingly good and indicates that we are observing a crystallinity effect.

Both the x-ray and DLI curves show only a little change in crystallinity up to about 100°C. Nevertheless, temperature has an adverse effect on tensile properties of this very highly crystalline polymer in the 25–100°C. range. Thus, the tensile strength of poly-3-MB drops from the 5000 psi range at 25°C. to about 1800 psi at 100°C. This behavior reflects the onset of motion associated with the glass transition. In ex-
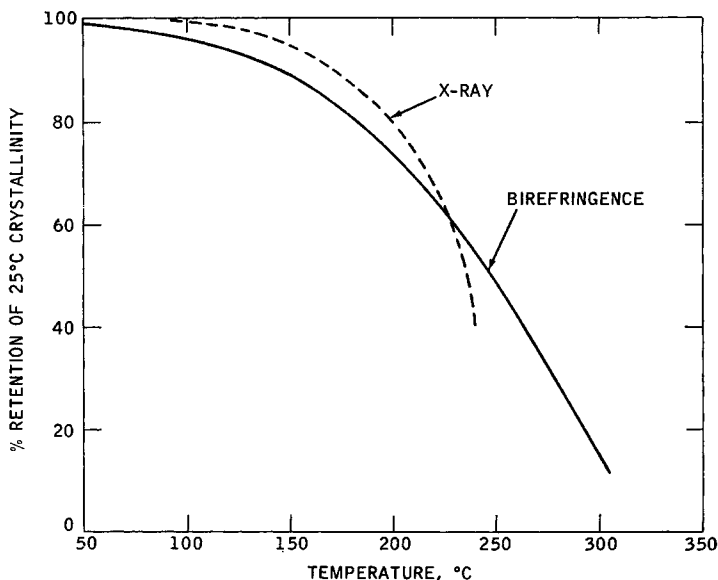
Fig. 6. Retention of crystallinity vs. temperature. X-ray data from Natta et al.[14]

amining the molecular processes leading to the glass transition relaxation, it is important to consider the barrier to main chain motion: namely (1) the energy barrier to rotation about the C–C bonds of the main chain as reflected in molecular chain stiffness and (2) the barrier due to interaction with other molecules. Here the bulkiness of the side group, intermolecular distances, and even intercrystallite distances become important. Accepting the definition for the glass transition as that temperature region in which the main polymer chain acquires large-scale mobility does not eliminate the distinct possibility that there is an interaction between the mobility of the bulky side chain and large-scale chain mobility.

It should be noted that the shape of the DLI–temperature curves were the same for all fully crystallized poly-3-MB samples, independent of spherulite size and thermal history. Most often a freshly molded poly-3-MB film (5–10 mils) gave the curve shown in Figure 4 when studied by DLI. Some films, however, gave anomalous DLI curves. On aging these films for about 3–5 hr., the DLI curves again resembled that in Figure 4. The data are shown qualitatively in Figure 7. There are a number of circumstances that could lead to the behavior shown in Figure 7. Thus the high mold shrinkage of poly-3-MB could promote the development of "thermal" stress in the compression-molded film. This stress, if it were present, would contribute to the total birefringence of the polymer films. The data in Figure 7 could also be explained on the basis of a metastable form crystallizing first from the melt and subsequently being converted to the more stable form. Alternate possible causes for the observed phenomenon involve changes in form birefringence, degree of
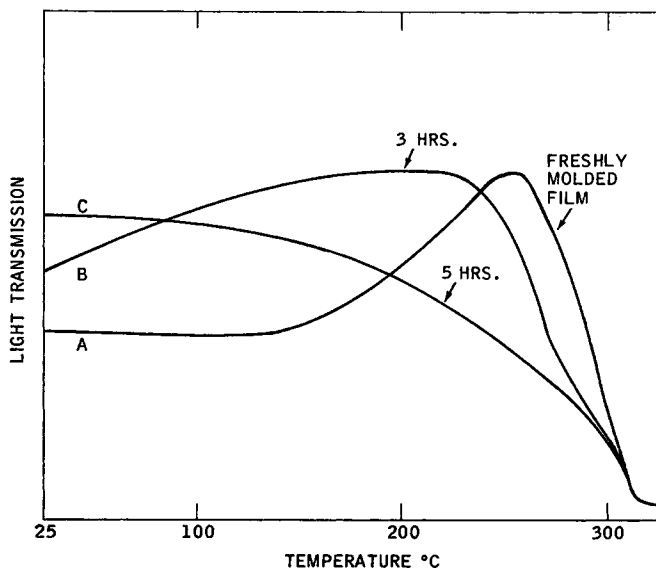
Fig. 7. Qualitative DLI curves.

crystallinity, or total scattering. In any case, it is extremely interesting that the changes in the shape and position of the DLI curve can occur in as short a period as 3–5 hr. at room temperature, in spite of the relatively low mobility that might be expected from the sterically hindered, high melting, highly crystalline poly-3-MB at temperatures 25°C. or more below the glass transition temperature.

When the poly-3-MB was extracted with Isopar H at 178°C. for 24 hr., about 4 wt.-% of the polymer was removed. The extractable material was amorphous when analyzed by x-ray. It may have contained low molecular weight polymer. The removal of this material which could serve as a plasticizer to increase molecular mobility accentuated the effects shown in Figure 7. When curve A was obtained with the extracted sample of poly-3-MB, aging the film for as long as 7 days at room temperature did not give curve C. However, repeated melting and cooling of the freshly prepared film of extracted poly-3-MB greatly accelerated the conversion. Once the normally observed curve was obtained, repeated melting and cooling on the hot stage did not change the shape or position of the DLI–temperature curves.

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Résumé

On a étudié les propriétés physiques et mécaniques ainsi que le comportement à la cristallisation du poly-3 méthyl-1 butène (poly-3MB). Le comportement à l'état fondu du poly-3MB a été étudié par la méthode de l'intensité de lumiere polarisée (DLI). Ces études de biréfringence montrent que le début du mouvement dans la phase cristalline du poly-3 MB a lieu aux environs de 100°C (plus de 200°C, endessous du point de fusion). Ces études montrent aussi qu'un mouvement moléculaire limité peut se produire a température de chambre, par exemple a environ 25°C, en dessous de la température de transition vitreuse du poly-3 MB.

Zusammenfassung

Eine Untersuchung der physikalischen und mechanischen Eigenschaften sowie des Kristallisationsverhaltens von Poly-3-methyl-1-buten (Poly-3-MB) wurde durchgeführt. Das Schmelzverhalten von Poly-3-MS wurde mit dem Verfahren der Messung der Intensität des depolarisierten Lichts untersucht. Die Doppelbrechungsmessungen lassen den Eintritt in der Bewegung in der kristallinen Phase von Poly-3-MB bei etwa 100°C erkennen. (Mehr als 200°C unterhalb des Schmelzpunkts.) Die Untersuchungen zeigten auch, dass begrenzte Molekülbewegung bei Raumtemperatur auftreten kann, d.i. etwa 25°C unterhalb der Glasumwandlungstemperatur von Poly-3-MB.