**Table I**
**Characterization of Polymers and Solvents**

| | | |
|---|---|---|
| Polymer code no. | 177-4 | 235-2 |
| $\bar{M}_i \times 10^{-6}$ | 0.42 | |
| $\bar{M}_w \times 10^{-6}$ | 0.45 | 1.44 |
| $[\eta]$, toluene, ml/g, 25° | 113 | 298 |
| $[\eta]$, PDMS solvent, 25° | 54.5 | 189 |
| Solvent code[a] | DC-200, 20 cs | DC-200, 5 cs |
| $\eta_s$, 25.0°, P | 0.183 | $0.048_5$ |
| $\rho_s$, 25.0°, g/ml | 0.949 | 0.920 |

[a] The second number is the nominal viscosity in centistokes.

**Table II**
**Hydrodynamic Interaction Parameters and Relaxation times**

| | | |
|---|---|---|
| $M_w \times 10^{-6}$ | 0.45 | 1.44 |
| $h^*$ | 0.15 | 0.15 |
| $S_1$ | 2.11 | 2.11 |
| Log $\tau_{01}$ (sec) | −4.06 | −3.60 |
| Log $(\tau_{01}/\eta_s)$ | −3.32 | −2.29 |
| $\alpha_\eta$ | 1.00 | 1.25 |
| $\alpha_\eta h^*$ | 0.15 | 0.19 |

creasing frequency as usually observed; this behavior is consistent with the hypothesis that the longest relaxation time is much more strongly concentration dependent at very low concentrations than are the other relaxation times.[2]

The extrapolated values are reduced to $[G']_R = [G']M/RT$ and $[G'']_R = [G'']M/RT$, with $M$ taken as the weight-average value, and plotted logarithmically against $\omega\eta_s[\eta]M/RT$ in Figure 1. These coordinates are convenient for comparison with the shapes of theoretical curves.[9] The points were matched to logarithmic plots of $[G']_R$ and $[G'']_R$ *vs.* $\omega\tau_{01}$, where $\tau_{01}$ is the longest relaxation time at infinite dilution, calculated from the Lodge-Wu evaluation[6] of the Zimm theory with $N = 300$ (number of submolecules) and various values of $h^*$ (hydrodynamic interaction parameter). The match involves a horizontal shift of the abscissa to make $[G'']_R$ coincide at low frequencies; this shift is log $S_1$, where $S_1 = \Sigma(\tau_{0p}/\tau_{01})$, the $\tau_{0p}$ being the individual relaxation times evaluated for a particular $h^*$. The theoretical curves are drawn in Figure 1 and the values of $h^*$, $S_1$, and $\tau_{01}$ ($= \eta_s[\eta]M/RTS_1$) are given in Table II. The curves agree with the data quite well, though the uncertainty in $h^*$ is at least ±0.03. The deviation in $[G']_R$ at low frequencies for the sample of higher molecular weight is in the direction to be expected from a small degree of molecular weight heterogeneity.

In previous work on linear polymers,[3] $h^*$ has been found to be approximately inversely proportional to $\alpha_\eta$, where $\alpha_\eta{}^3$ is the ratio of intrinsic viscosities in a particular solvent and in a $\Theta$ solvent. For PDMS, the $\Theta$-solvent intrinsic viscosity can be calculated from data reviewed by Stockmayer and Kurata,[10] for example, in methyl ethyl ketone at 20°, as 54.2 and 97.2 ml per g, respectively; the latter agrees also with a value measured in bromocyclohexane at the Dow Corning Corp. From these, the values of $\alpha_\eta$ given in Table II are obtained. It appears curious that the 20-cs oligomeric PDMS used for the polymer of lower molecular weight is a $\Theta$ solvent, whereas in the 5-cs oligomer used for the other polymer $\alpha_\eta$ is greater than unity. However, it is generally accepted[11] that a polymer molecule surrounded by others of its kind has unperturbed dimensions, and the average molecular weight in the 20 cs solvent may be sufficiently high to provide these conditions.

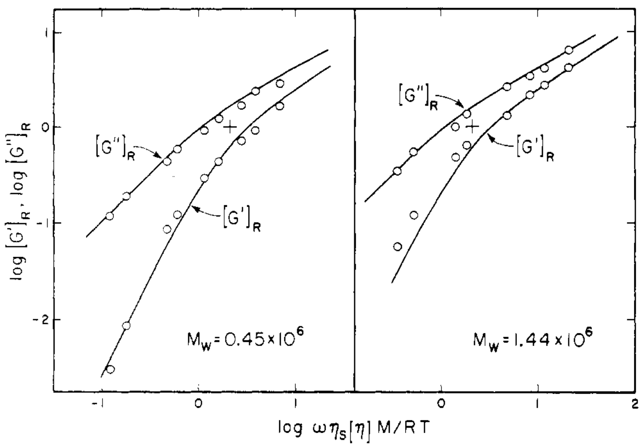

**Figure 1.** Reduced intrinsic storage and loss moduli plotted logarithmically against $\omega\eta_s[\eta]M/RT$ for samples with weight-average molecular weights as indicated. Curves drawn from Zimm theory evaluated by Lodge and Wu with $N = 300$, $h^* = 0.15$. At cross, $\omega\tau_{01} = 1$.

The product $\alpha_\eta h^*$ is, for both samples, somewhat smaller than the average of 0.21 previously observed,[3] but the differences are not sufficiently outside the uncertainty of curve fitting to judge their significance. In any case, the predictions of the Zimm theory, which are rather insensitive to the choice of the single adjustable parameter $h^*$, agree closely with the data both in absolute magnitude and in frequency dependence, providing additional evidence of the utility of the bead-spring model in this frequency range. Effects which are specific to the detailed chemical structure may be anticipated at higher frequencies.[1,12]

**Acknowledgment.** This work was supported in part by the Army Research Office (Durham), the National Institutes of Health, and the National Science Foundation.

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## On the Molecular Weight Determination of EPM and EPDM Rubbers

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The molecular characterization of copolymers of ethylene and propylene (EPR, EPM) and of terpolymers of these two and a third, diene, monomer (EPDM), often meets with problems. Recently, Baldwin and Ver Strate[1] in an extensive review of ethylene-propylene elastomers discussed the conflicting molecular weight values found for such polymers, and mentioned incomplete dissolution as a possible cause of the discrepancies. Dissolution at low temperature might not be effective enough in removing molecular aggregates and, in consequence, might cause abnormally large values of molecular weight to be found by light scattering. The problem is analogous to that indicated by

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(1) F. P. Baldwin and G. Ver Strate, *Rubber Chem. Technol.*, **45**, 709 (1972).

Table I
Molecular Weights $M_w$ of an EPDM Rubber Sample Measured by Light Scattering in Different Solvents for Different Dissolving and Measuring Circumstances

| Solvent | Dissolution | | Measuring Temp (°C) | $M_w \times 10^5$ | Remarks |
|---|---|---|---|---|---|
| | Time (hr) | Temp (°C) | | | |
| *n*-Heptane | 2 | 26 | 26 | 20 | Extrapolation to zero concentration |
| *n*-Heptane | 17 | 26 | 26 | 17 | Concentration = $1.4 \times 10^{-3}$ g/ml |
| | | | 71 | 10 | |
| *n*-Heptane | 70 | 26 | 26 | 5.7 | Concentration = $1.4 \times 10^{-3}$ g/ml measured in the same cell for 1 hr at alternating temperatures of 26 and 71° |
| | | | 72 | 3.2 | |
| | | | 26 | 3.4 | |
| | | | 71 | 3.3 | |
| | | | 26 | 3.3 | |
| | | | 71 | 3.2 | |
| | | | 26 | 3.4 | |
| | | | 71 | 3.3 | |
| *n*-Heptane | 17 | 71 | 72 | 4.0 | Concentration = $1.4 \times 10^{-3}$ g/ml |
| | | | 26 | 4.5 | |
| *n*-Heptane | 70 | 71 | 71 | 3.9 | Concentration = $1.4 \times 10^{-3}$ g/ml |
| | | | 26 | 4.1 | |
| $\alpha$-Chloronaphthalene | 2 | 120 | 123 | 3.7 | Extrapolation to zero concentration |
| $\alpha$-Chloronaphthalene | 2 | 120 | 123 | 3.4 | Extrapolation to zero concentration |
| $\alpha$-Chloronaphthalene | 72 | 120 | 123 | 3.2 | Extrapolation to zero concentration |

Schreiber and Waldman,[2,3] who found too high values for the $M_w$ of polyethylene from light scattering in $\alpha$-chloronaphthalene solution below 140°. These authors attributed this phenomenon to aggregation caused by persistence of chain entanglements and to crystallites or ordered aggregates of the polymer. Morimoto and Okamoto[4] ascribe an abnormal Zimm plott of an EPMD sample in $\alpha$-chloronaphthalene to molecular aggregation taking place between ethylene sequence parts along the polymer chains.

Baldwin and Ver Strate's suggestions instigated us to carry out a critical review of the dissolution and measuring procedures used in this laboratory. The value of the weight-average molecular weight $M_w$ found by light scattering indeed proved to depend strongly on the dissolution temperature and, to a smaller extent, on the measuring temperature. In determining $M_n$ from membrane osmometry at 115° in 1,2,4-trichlorobenzene, and $[\eta]$ from the viscosity in decalin at 135°, we did not encounter such problems, probably because these measurements are carried out at relatively high temperatures and, in addition, are much less affected by molecular aggregates. (Since most aggregates have a compact structure, they hardly influence the viscosity of the solution.)

The problem with light-scattering measurements is illustrated here with reference to representative data on a laboratory sample of Keltan EPDM rubber with an $M_n$ value of $5.9 \times 10^4$, an intrinsic viscosity $[\eta] = 1.72$ dl/g in decalin of 135° (shear stress 10 dyn/cm$^2$), and a propylene content of 31% by weight. An *n*-hexane solution of the sample was subjected to centrifugation, as a usual procedure to free it from any possible gel. The polymer, evaporated to dryness, was then dissolved in the solvent chosen and subsequently filtered over a commercial 5 $\mu$ Millipore filter. Dibutyl-*p*-cresol was used as an antioxidant. This is a rather extreme example, which, being characterized by a relatively poor solvent and a relatively low propylene content of the polymer, clearly demonstrates the present effect. The results are listed in Table I.

Scattered light intensity measurements performed in the usual way on an *n*-heptane solution of the sample prepared by stirring at 26° during 2 hr gave an $M_w$ value of $2.0 \times 10^6$. Experiments were carried out also with 0.14% solutions upon various temperatures and times of dissolution and at various measuring temperatures. In these cases the relevant $M_w$ values were calculated without extrapolation to zero concentration. The error, introduced hereby is small in comparison with the effects to be measured.

Upon longer dissolution times (17 hr) $M_w$ decreases. This has been verified up to a dissolution time of 70 hr. An increase of the measuring temperature also leads to a lower $M_w$ value. A series of measurements at alternating temperatures of 26 and 71° revealed that the decrease of $M_w$ with higher temperatures is irreversible in the time frame used for these experiments; this suggests that higher temperatures tend to facilitate dissolution. Dissolution under stirring at higher temperatures, however, is much more effective.

Finally, some measurements were performed on the sample dissolved in $\alpha$-chloronaphthalene at 123°, after dissolution times of 2 hr (duplicate runs) and 72 hr. In these cases normal Zimm plots yielded relatively low $M_w$ values.

Baldwin and Ver Strate's suspicion is strongly supported by these data. The data are representative; similar effects have been observed with a large number of other EPDM samples. An increase in dissolution temperature, dissolution time, and measuring temperature each proved to have a lowering effect on the $M_w$ value.

We can explain these phenomena by assuming that the dissolution at low temperatures, although leading to an optically clear solution, might not be effective enough in removing persistent chain entanglements. Generally at about 120° (in $\alpha$-chloronaphthalene) a true solution is obtained; longer dissolution times and higher dissolution temperatures do not decrease the $M_w$ values. With one series of commercial EPDM's however (Nordel, E. I. du-Pont de Nemours & Co.), dissolution at 120° was not sufficient, and it was necessary to dissolve the samples at 140°. (These samples had neither a deviating low specific propylene content (*ca.* 40% by weight), nor a relatively high crystallization temperature.)

An important point to be considered in these procedures is the possibility of polymer degradation at high temperatures. However, in view of the assymptotical approach of $M_w$ to some end value, degradation at these temperatures must be considered improbable. Only at 170° irreproducible results are obtained, suggesting the occurrence of degradation, whether or not combined with cross-linking. It can be difficult, however, to find out at what temperature the aggregates are removed and degradation starts. Also very strong agitation of the solution might cause degradation of the polymer.

In the light of the data obtained from these and further experiments, the authors have come to the conclusion that a suitable procedure for $M_w$ determination of EPM and EPDM rubbers goes as follows. Without it being attempted to remove any gel beforehand, the sample is dissolved by gently stirring it in $\alpha$-chloronaphthalene in an inert atmosphere, at 140°, with a suitable antioxidant added to it. The dissolution time is 2 hr; in the case of slowly dissolving samples, however, stirring must be continued up to 1 hr after the sample has visually solved. After that, the

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(2) H. P. Schreiber and M. H. Waldman, *J. Polym. Sci., Part A*, **2**, 1655 (1964).

(3) H. P. Schreiber, *Polymer*, **13**, 78 (1972).

(4) M. Morimoto and Y. Okamoto, *J. Appl. Polym. Sci.*, **16**, 2795 (1972).

sample is filtered through a 5 μ Millipore filter at 140° and immediately measured at 140°.

**Acknowledgement.** The authors are indebted to Drs. H. C. Booij and R. Koningsveld for helpful discussions. Thanks are due also to Drs. F. P. Baldwin and G. Ver Strate, who were kind enough to put the manuscript of ref 1 at Dr. Booij's disposal prior to publication. The measurements were skilfully performed by Mrs. E. M. L. Nijsten.

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## Microscopy of Isotactic Polypropylene Crazed and Fractured in Liquid Nitrogen

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*Received March 19, 1973*

Crazing is commonly associated with glassy amorphous polymers.[1,2] The crazes are formed by highly localized drawing of the unoriented material. Such plastic deformation yields high molecular orientation of the material in the crazes. These are relatively thin, a few microns in the stress direction, but can grow laterally as long as the local stress concentration at the sharp tip of the craze is sufficient for propagation. Under homogeneous, one-dimensional tensile stress, each craze may extend through the whole cross-section of the sample, the craze plane being perpendicular to the stress direction. The growth of craze thickness occurs mainly by progressive plastic deformation of the already crazed material and not so much by conversion at the craze boundary of the unoriented polymer into crazed material. This thickness growth implies that the bulk density in the craze diminishes by longitudinal void formation. In this state, the craze consists of numerous fibrils bridging the gap between the uncrazed bulk material on each side of the craze. The high molecular orientation in the fibrils gives them a high tensile strength; therefore, the craze does not significantly weaken the sample although eventually a crack will nucleate in a craze and not, as a rule, in uncrazed material. The sequence of events leading from crack nucleation to crack propagation, and the important role played by the craze, have been described in great detail by Kambour[3] and by Murray and Hull.[4-8]

A few reports in the literature indicate that crazing can occur in crystalline polymers as well.[9-14] In particular, crystalline polypropylene (PP) was shown by van den Boogaart[11] to craze at room temperature and above. We recently observed extensive crazing in smectic polypropylene at low temperatures, in the range between −210 and 0°, and a pronounced dependence of crazing on the gaseous environment.[14] This last effect seems to be closely related to the environmental stress crazing of amorphous polymers recently reported by Parrish and Brown.[15]

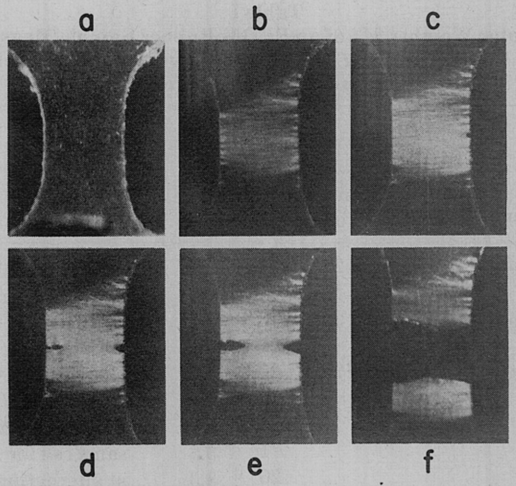

**Figure 1.** Optical micrographs at low magnification of crazing in PP while strained in liquid nitrogen (a) 0%, (b) 19%, (c) 33%, (d) 35%, (e) 49%, and (f) after rupture at approximately 50% strain. Illumination at about 45° to optical axis from behind the sample. Width of the sample was 0.5 cm.

The main feature of our observations was a dramatic increase of strain to break and of craze density at temperatures close to the boiling point of the surrounding gas (nitrogen, oxygen, carbon dioxide, and, as found recently, argon), *i.e.*, at high activity of the gas. In nitrogen at 1 atm the material, comparatively brittle between −50 and −140°, showed increasing toughness, ductility, and extent of crazing below −140°. The strain to break became a maximum at −196°, the boiling point of nitrogen, and did not change perceptibly down to the solidification point of nitrogen, the lowest temperature of our investigation. Thus, the extent of crazing and the concomitant strain to break seem to be related to the activity of the gas. When increasing the temperature above the boiling point, the gas activity rapidly decreases and so does the strain to break. At −140° no effect of the nitrogen is observable. The strain to break has reached the plateau value identical with that observed with the sample loaded under vacuum. Moreover, the vacuum data are identical with those in helium. Under atmospheric pressure, the activity of helium gas at liquid nitrogen temperatures is indeed so low that the environmental effect on plastic deformation of crystalline polypropylene can be neglected.

Isotactic PP in the smectic modification, crazed and fractured in liquid nitrogen, not only shows strain to break unusually high for a homopolymer, up to 60%, but also rather unique features of the fracture surface when examined by optical and scanning electron microscopy. Such microscopical observations are reported below.

As in the previous experiments,[14] a commercial film of isotactic polypropylene 0.125 mm thick (made by the Rexall Chemical Co.) was used. According to X-ray diagrams, the crystallites are in the so-called smectic form and randomly distributed, *i.e.*, the film is isotropic. Micrographs of crazing of smectic PP samples in liquid nitrogen are shown in Figure 1 as obtained at gradually increased strain, up to the final fracture of the specimen. The quality of the pictures is relatively poor since they were obtained by observation inside the low-temperature Dewar so that the light had to pass through two glass

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