Solution Properties and Molecular Structures of EPM and EPDM

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Synopsis

The solution properties of EPDM were investigated based on EPM as a model compound of linear molecules. The glass transition temperature and the propylene content in EPDM were measured as a function of the molecular weight. Good agreement between the solution behaviors of EPM and EPDM was observed. This was correlated to change not only in the propylene composition but also in the monomer sequence distribution.

INTRODUCTION

One of the important requirements for commercial elastomers is good processing properties. Molecular structures have a profound effect on the processing process and the rheological properties. Long-chain branching, molecular weight distribution, and the distribution of monomer sequences along the polymer chain are of particular importance in molecular structure terms.

The monomer sequence distribution has been evaluated by reactivity ratios for ethylene–propylene (EPR) copolymerization with soluble Ziegler catalysts.[1–7] It was pointed out that the composition of EPR undergoes a sigmoidal increase in ethylene content as one passes from the low to high molecular weight portion of the distribution.[5] Michajlov reported that the distribution of EPR chain fragments according to length may be correlated to the blockiness of ethylene in the polymer chain.[7]

Tokita proposed that EPDM in general is branched, based on a comparison of the zero shear viscosity of EPDM with that of the linear homologue of the same intrinsic viscosity.[8]

Commercial EPDM may exhibit differing monomer sequence distribution along the terpolymer chain, depending on the molecular weight. Therefore it is of considerable interest to obtain information on the monomer sequence distribution in EPDM, which affects the processing properties and the rheological behavior. We attempted to investigate the solution properties of commercial EPDM to elucidate the molecular structures of the terpolymer, assuming EPM as a linear molecule.

EXPERIMENTAL

Materials and Characterizations

Ethylene–propylene copolymer (EPM) was prepared by a soluble Ziegler catalyst of an alkylaluminum halide–vanadium salt type in a continuous-flow stirred reactor according to a procedure proposed by Cozewith et al.[5] The ethylene–propylene–ethylidenenorbornene terpolymers (EPDM) used were commercial samples obtained in Japan.

Structures parameters are shown in Table I.

TABLE I
Structure Parameters of EPM and EPDM

Sample	$M_n{}^a$	$M_w{}^a$	Q^b	C_3, moles[c]	I.V.[d]	$[\eta]$
EPM						
A	58,500	157,000	2.68	27.6	—	2.82
B				57.9	—	
EPDM						
C	34,900	73,700	2.11	34.9	8.2	1.69
D	30,600	112,000	3.64	37.1	7.5	1.59
E	21,500	129,000	6.01	40.7	9.7	1.72

[a] The molecular weight values were derived from GPC calibration curves by the usual method.
[b] The ratio of weight- to number-average molecular weight.
[c] Propylene mole-%.
[d] Iodine values.

The molecular fractionation was done by the usual precipitation method at 30°C, using toluene as good solvent and isopropanol as poor solvent. The gel permeation chromatography experiments were carried out on a Shimazu GPC 1A equipped with four columns (1×10^6, 1×10^5, 1×10^4, and 1×10^3 Å) in o-dichlorobenzene at 110°C. The weight-average molecular weights were measured in α-chloronaphthalene at 125°C by a Shimazu light-scattering photometer PG 21. The glass transition temperature (T_g) values were measured by a Perkin Elmer Model DSC 1B. A Hitachi grating infrared spectrometer EPI-G3 was used for determination of the composition of propylene and the amount of ENB expressed in iodine values according to the procedures proposed by Wei[9] and Levine et al.,[10] respectively. Intrinsic viscosities were measured for all samples in xylene at 70°C.

RESULTS

Zimm Plots of Data Obtained by Light-Scattering Photometer

The Zimm plots of EPDM sample E are unusually distorted, and the A_2 value is extremely small (Fig. 1, Table II), while EPM and the other

TABLE II
Parameters of Nonfractionated Samples, Calculated from the Zimm Plots

Sample	$\bar{M}_w$	A_2[a]	$\langle S^2 \rangle^{1/2}$,[b] Å
EPM			
A	356,000	7.83×10^{-4}	460
B[c]			
EPDM			
C	224,000	6.93×10^{-4}	322
D	277,000	5.43×10^{-4}	398
E	455,000	1.78×10^{-4}	414

[a] Second virial coefficient.
[b] Mean square radius of gyration.
[c] No measurement for small amount of sample.
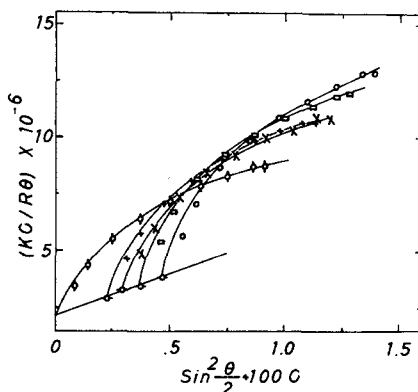
Fig. 1. Zimm plots of EPDM sample E.

EPDM samples show the usual Zimm plot and the usual A_2 value. Distortion in the Zimm plots can be observed only at the high molecular weight region.

Fractionation

Fifty fractions were originally collected and adjacent cuts were combined to obtain 15–20 equal portions. Fractionation of copolymer heterogeneous in compositions raises problems in efficiency. Q values of each fraction varied no more than 1.5 ± 0.2. It is known that efficiency of fractionation may be affected not only by the molecular weight but also by the copolymer composition. Thus, a plot of log ($[\eta] \times \bar{M}_w$) versus log $[S^2]$ was carried out in Figure 2, according to the Flory-Fox equation. All points for EPM and EPDM were fixed in a straight line with a slope of $\frac{3}{2}$ in the experimental errors. This could indicate high efficiency in the fractionation procedures.

Composition

A plot of the propylene composition in the polymer chain versus $[\eta]$ is shown in Figure 3. Among the three types of EPDM, the propylene com-
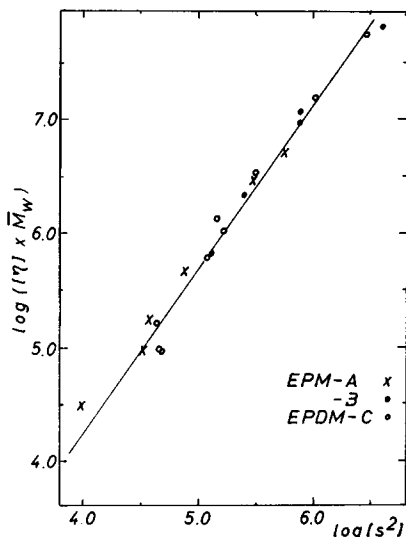
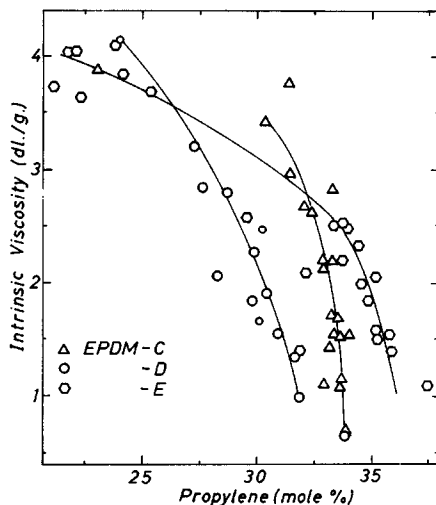Fig. 2. Plot of log ($[\eta] \times \bar{M}_w$) vs. log $[S^2]$.

Fig. 3. Plot of propylene (mole-%) vs. $[\eta]$.

position in the polymer tends to decrease as $[\eta]$ increases, leading to an irregular sequence distribution of ethylene as a function of molecular weight. For the three samples of EPDM the compositional spread is greater than $\pm 10\%$ about the mean. The compositional spread of EPDM sample E is extremely great relative to EPDM samples C and D.

T_g Values

Analysis of the three types of EPDM for the glass transition temperature (T_g) by differential scanning calorimetry (DSC) revealed a gradual rise with
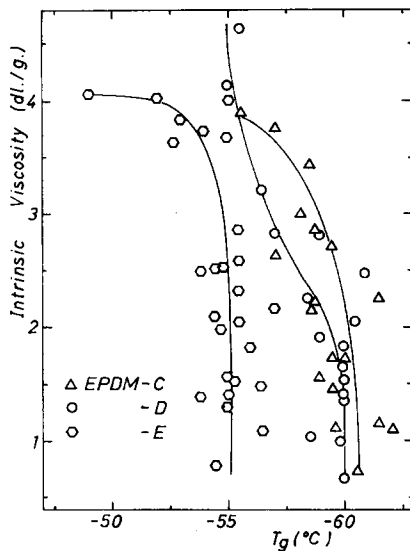
Fig. 4. Plot of T_g vs. $[\eta]$.
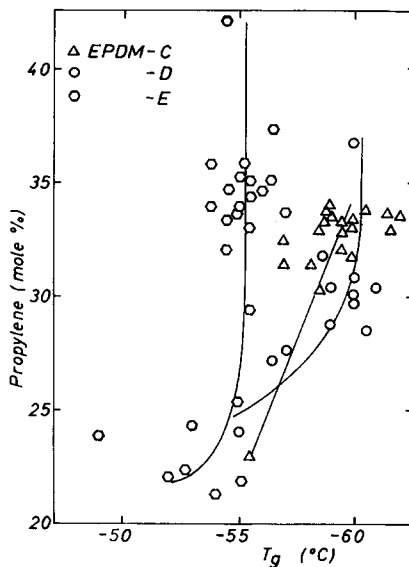
Fig. 5. Plot of T_g vs. propylene composition.

an increase in $[\eta]$ and ethylene content in the polymer (Figs. 4 and 5). The T_g values of EPDM sample E are relatively a few degree higher than those of EPDM samples C and D.

Sequence of Length Distribution

The fraction of each methylene sequence was determined according to the infrared spectrum method proposed by Bucci and Simonazzi.[11] As a re-

TABLE III
The CH₂ Content in Various Sequences in EPDM Sample Eᵃ

Fraction no.	$[\eta]$	T_g, °C	C_3, mole-%	g_1	g_2	g_3	g_4	g_5
1	4.00	−55.1	21.9	8.8	0	0	4.1	87.1
2	3.73	−54.0	21.3	9.8	0	0	3.3	85.9
3	3.64	−52.7	22.4	10.5	0	0	17.2	72.3
4	2.58	−55.5	29.5	17.8	1.5	0	10.2	67.1
5	2.53	−54.9	33.7	23.8	2.5	7.2	2.9	63.7
6	2.49	−53.8	34.0	24.5	3.3	2.0	9.4	60.9
7	2.09	−54.5	32.1	21.3	0.9	0.6	15.5	61.6
8	1.82	−56.0	34.8	23.5	3.9	2.4	9.1	61.1
9	1.48	−56.4	35.2	24.9	4.5	2.4	7.2	60.0
10	1.39	−53.8	35.8	24.6	5.6	2.9	13.7	53.2
11	1.09	−56.5	37.4	24.8	3.3	8.9	7.5	55.5
12	0.78	−54.5	42.2	27.1	6.8	6.9	18.3	40.8

ᵃ Refers to $g_n = \dfrac{\text{grams CH}_2}{100 \text{ g}}$ corresponding to the $(CH_2)_n$ sequences, with $n = 1, 2, 3, 4$, and more than 5.

sult, it was shown that the fraction over five methylene linkages, g_5, increases with increasing $[\eta]$, while the fraction of one methylene linkage which is responsible for the head-to-tail bonding of propylene decreases with increasing $[\eta]$ (Table III).

Since this infrared analysis method can be applied to EPM in the absence of the third component, the above-obtained absolute values involve some errors due to the contribution from absorbance of ethylidene norborene (ENB). Even if the ENB absorbance effect is fully compensated, the value of g_5 will be much higher than the uncompensated values. Furthermore, since the ENB content in EPDM does not vary considerably with molecular weight, the obtained results would permit to discuss the monomer sequence distribution along the polymer chain.

The crystal fraction in the whole nonfractionated three samples of EPDM could not be detected by x-ray analysis.

Plot of Log $[\eta]$ Versus Log $\bar{M}_w$

The three types of EPDM gave a curvature at the high molecular weight region which may be related to long-chain branching on the EPDM backbone (Fig. 6). However, it is surprising that it deviates from the linearity for EPM, which could be treated as a model compound of the linear molecule (Fig. 6).

DISCUSSION

As seen in Figure 6, the plot deviates from linearity at the molecular weight range of about 10^5. It is well known that for a branched polymer the hydrodynamic volume decreases by the g-factor introduced by Zimm and Stockmayer.[12] It is somewhat surprising to obtain the same tendency
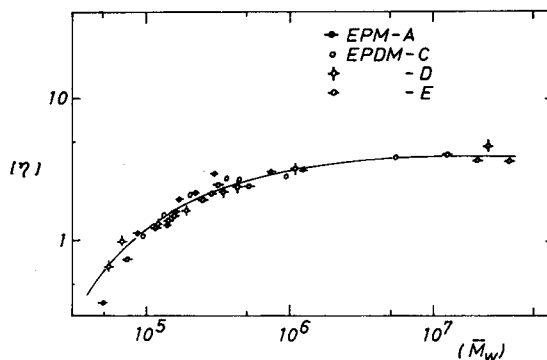
Fig. 6. Plot of log $[\eta]$ vs. $\bar{M}_w$.

for EPM in a plot of log $[\eta]$ versus log $\bar{M}_w$. The question now arises if such a deviation is due to a decrease in the hydrodynamic volume, leading to the branching effect. It is hard to imagine a branched molecule for EPM. Therefore, we must find the reason why this deviation is observed in all of the plots.

It was reported that the composition of EPM undergoes a sigmoidal increase or a gradual increase in ethylene content with increasing molecular weight of copolymer catalyzed by VCl_4–Et_2AlCl or $VOCl_3$–Et_2AlCl, respectively.[5] The deviation behavior from a linearity for EPM sample A in Figure 6 could be attributed to the systematic variation in ethylene content, leading to the long ethylene sequence distribution as an increase in molecular weight.

We may note, in particular, the very characteristic differences in the Zimm plots and A_2 values between EPDM sample E, EPM, and other types of EPDM. When the concentration is high, or when the polymer has a wide molecular weight distribution, the plots may consist of downward curvatures.[13,14] Special difficulties are encountered with solutions of polyelectrolytes and with aggregated molecules.[15] Matsuo reported that the Zimm plots of poly(vinyl alcohol) are unusually distorted in the presence of microgels.[16] It can be assumed that this is not due to polydispersity of the EPDM sample E, because of the carefully fractionated sample. It might be attributed to the molecular aggregation between ethylene sequence parts along the high molecular weight chains in connection with a decrease in slope (drawn between the varying concentration) as the angle decreases. Since the g_5 values increase with increasing molecular weights, it is clear that the molecular structure tends to increase the ethylene sequence length in the high molecular weight region. We were unsuccessful in quantitative separations of the branching effect and the ethylene sequence distribution effect on the solution behavior of EPDM in this investigation. If the branching effect of EPDM is involved in a plot of log $[\eta]$ versus log M_w, a greater deviation from linearity should be observed for EPDM than for

EPM sample A. However the fact that the solution behaviors of both EPM and EPDM are the same indicates that the branching effect of EPDM in the molecular structure is small relative to the ethylene sequence distribution effect. This disagrees with the result in which molecular structure of EPDM consists of long-chain branching due to the presence of the diene monomer.[8]

The T_g values of three types of EPDM reveal a systematic variation with change in the composition and the molecular weight (Figs. 4 and 5). This could be attributed to an increase in ethylene content and in molecular weight.

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