

ASSOCIATION OF EPDM MOLECULES IN SOLUTIONS

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Abstract—EPDM terpolymers could form gels in semi-dilute solutions in benzene and toluene. Viscometry indicates that association of EPDM molecules takes place in these solvents over a temperature range where a gel does not form. The extent of this association decreases with increasing content of propylene units and with increasing temperature.

INTRODUCTION

Dilute solutions of homopolymers and copolymers of ethylene are well known to form thermoreversible gels due to microcrystallization [1]. This phenomenon received a great deal of attention especially after high modulus fibres had been prepared by drawing polyethylene gels.

The existence of microcrystallites is not sufficient for gel formation. It is necessary for the macromolecules to be incorporated in more than one crystallite and for the extent of such incorporation to be large enough to form an overall network. The temperature is the major factor for the formation of crystallites but it is the concentration which mostly determines whether these crystallites act as junction points and whether the crosslinking leads to gelation.

Viscometric data presented here show that molecules of ethylene copolymers, specifically, ethylene-propylene-diene terpolymers (EPDM), associate even in very dilute solutions. This phenomenon is discussed in terms of the ability of the copolymers to crystallize in solutions.

EXPERIMENTAL PROCEDURES

Samples

Commercial samples of terpolymers of ethylene, propylene and a small amount (2–5 mol%) of diene monomer (ethylidene norbornene or dicyclopentadiene) (EPDM) were used (samples designated A, B, C). Sample C was fractionated by precipitation from ca 1% hexane solution with a mixture of methanol and acetone (30/70 by vol) as precipitant. Fractionation was carried out in the usual manner and 11 fractions were obtained. Only the first and the tenth fraction (C1 and C10) were used in this study. Samples have been characterized by viscometry (intrinsic viscosity $[\eta]$), osmometry (number-average molecular weight M_n and second virial coefficient A_2) and $^1\text{H-NMR}$ spectroscopy (content of propylene monomeric units, x_p). The results are summarized in the table.

Viscometry

Viscosity measurements were made in an Ubbelohde capillary viscometer adapted for subsequent dilution; the flow times were recorded opto-electrically using a home-made apparatus. The temperature was constant within 0.03° . The dimensions of the viscometer were such that

viscometric corrections were negligible. The concentration range was chosen so that t/t_0 (t and t_0 being the flow times of solution and solvent respectively) was between 1.1 and 1.8. The Heller method [2] was used in the determination of $[\eta]$ and of the Huggins constant, k_H .

RESULTS AND DISCUSSION

Methods for the estimation of the Huggins viscosity coefficient

Our finding that EPDM molecules associate in dilute solutions is based on an analysis of the Huggins coefficient, k_H . It is defined by the equation

$$(\eta/\eta_0 - 1)/c = [\eta] + k_H[\eta]^2c + k_2[\eta]^3c^2 + \dots \quad (1)$$

where η and η_0 are, respectively, the viscosity of solution and solvent, $[\eta]$ is the intrinsic viscosity, and c is the mass concentration. A semi-empirical equation has been proposed [3] to describe this dependence,

$$k_H = 0.5/\alpha_n^4 + 0.3(1 - 1/\alpha_n^2), \quad (2)$$

where $\alpha_n^3 = [\eta]/[\eta]_0$ is the viscosity expansion factor, $[\eta]_0$ being the intrinsic viscosity under theta conditions.

The $[\eta]$ and k_H values are currently estimated from the intercept and slope, respectively, of the Huggins plot, $(\eta/\eta_0 - 1)/c$ vs c . This procedure neglects the contribution of the third term on the right-hand side of equation (1). However, this may lead to serious errors in $[\eta]$ and, particularly, k_H . On the other hand, the Heller plot [2] based on the equation

$$\begin{aligned} [c/(\eta/\eta_0 - 1) + c/\ln(\eta/\eta_0)] \\ = 1/[\eta] - (k_H - 1/4)c + \dots \end{aligned} \quad (3)$$

has been shown [3] to take an approximate account of the term $k_2[\eta]^3c^2$, at least with polymer systems where $k_2 \leq k_H^2$.

Wolff *et al.* [4] found that, if the intrinsic viscosity of associated species is higher than that of non-associated molecules, the Huggins coefficient is increased by association. The authors started from the Huggins equation,

$$(\eta/\eta_0 - 1)/c = [\eta] + k_H[\eta]^2c \quad (4)$$

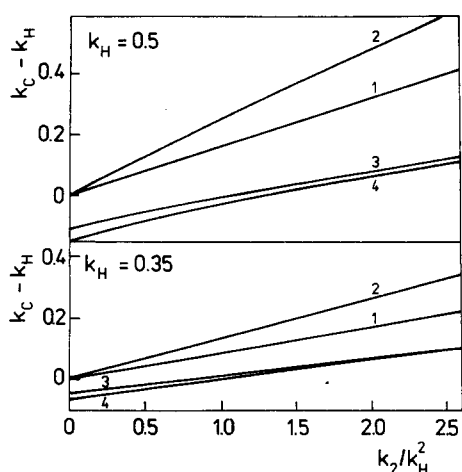


Fig. 1. Comparison of estimates of k_H by the Huggins and Heller plots (model calculations). ($k_C - k_H$) is the difference between the "experimental" and correct values of the Huggins coefficient. Huggins plot: narrow concentration range (line 1), wider concentration range (line 2). Heller plot: narrow concentration range (line 3) wider concentration range (line 4).

i.e. from equation (1) without the third term, but obtained a significant contribution to the third term. Hence, we must suppose that, with associating systems, k_2 could be higher than k_H^2 . Therefore we tested the reliability of the k_H values determined by the Huggins and the Heller plots with calculated data for systems where $k_2 \neq k_H^2$, i.e. for a wider range of conditions than in Ref. [3].

With $k_H = 0.35$ and 0.5 and $0 \leq k_2 \leq 2.5k_H^2$ substituted into equation (1), we calculated "experimental" values of $(\eta/\eta_0 - 1)/c$ for 11 equally distributed concentrations chosen so that the values of η/η_0 were 1.1 for the lowest and 1.8 (as usually recommended) or 2.6 for the highest concentration. The "experimental" values of the Huggins coefficient were determined by the least squares method with equations (3) and (4). The results are shown in Fig. 1. In all cases, the Heller method provided a better estimate of k_H than the Huggins plot. The only exception was for very low values of k_2 , i.e. $k_2 \rightarrow 0$, but this case is not met in practice. Hence, use of the Heller method was justified for the present system.

The Huggins coefficients for EPDM copolymers

Viscosity measurements of EPDM copolymers were carried out at 30° in benzene and 25° in toluene. Benzene has been reported [5, 6] to be a theta solvent for ethylene-propylene copolymers (EPM) with $x_p = 0.28$ and 0.50 ($\theta = 28^\circ$ and 19° , respectively). Values of the second virial coefficient (Table 1) show

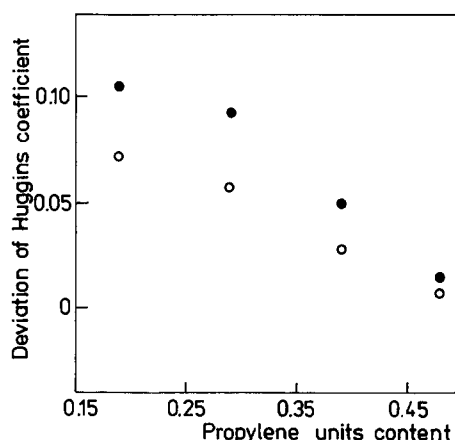


Fig. 2. Dependence of the deviation of the Huggins coefficient (Δk_H) on the composition of EPDM samples given by the molar content of the propylene unit x_p . Benzene at 30° , \bullet ; toluene at 25° , \circ .

that it is a poor solvent for EPDM of wider composition range even at 30° .

According to equation (2), we would expect k_H to be 0.5 at the theta temperature and less than 0.5 at $T > \theta$. We have however, found higher k_H values in benzene than those expected. In toluene, a good solvent, the Huggins coefficients were >0.35 , an approximate value for good solvents. With both systems, the differences exceeded the uncertainty of estimation. This behaviour indicates association of the EPDM molecules.

Wolff *et al.* [4] published equations for the difference in k_H values for associating and non-associating systems. However, they cannot be used here because the necessary details of association are not known.

We used the difference, Δk_H , between the experimental k_H value and that calculated by means of equation (2). The $[\eta]_0$ values were estimated using the semi-empirical Krigbaum equation [7]

$$[\eta] = [\eta]_0 + 0.5A_2M \quad (5)$$

from the data for benzene at 30° (Table 1).

Figure 2 shows Δk_H plotted against the content of propylene units and in Fig. 3 against temperature. They decrease with an increase in either x_p or T and become negligible at $x_p \cong 0.5$ or $T \cong 50^\circ$.

This finding can be compared with the rules for the crystallization and gelation of ethylene copolymers. Domcszy *et al.* [1] found that a higher content of pendant groups (C_2H_2 , CH_3COO) reduces the tendency to form gels and/or to crystallize. The dependence of Δk_H on composition for EPDM samples has a similar trend. We suppose that there is a close correlation between the ability to crystallize and

Table 1. Characterization of EPDM samples

Sample	$\bar{M}_n \times 10^{-4}$	x_p	$[\eta]_0^a$ (cm ³ /g)	$[\eta]_0^b$ (cm ³ /g)	A_2^b (mol cm ³ /g ²)
A	8.6	0.19	181	125	0.3
B	7.8	0.39	162	115	1.9
C1	9.1	0.29	189	111	0.8
C10	5.3	0.48	137	109	2.1

^aIn toluene at 25° .

^bIn benzene at 30° .

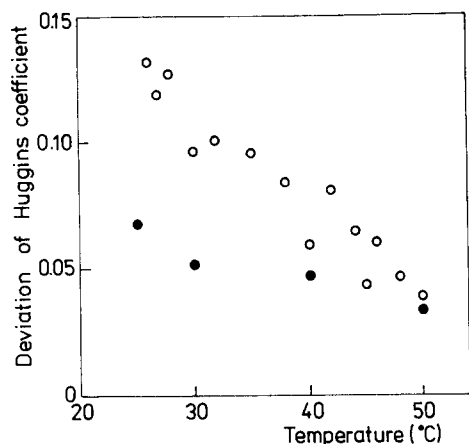


Fig. 3. Temperature dependence of the deviation of the Huggins coefficient (Δk_H) of EPDM sample A. Benzene, \circ ; toluene, \bullet .

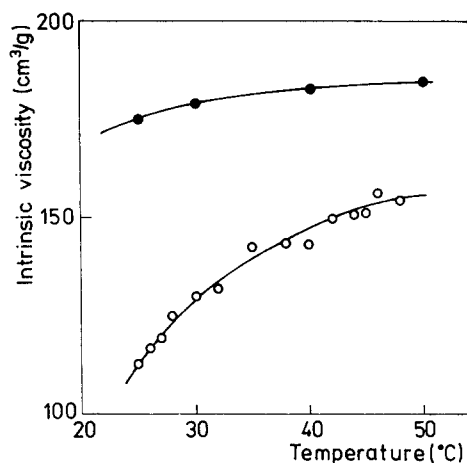


Fig. 4. Temperature dependence of the intrinsic viscosity of EPDM sample A ($x_p = 0.19$). Benzene, \circ ; toluene, \bullet .

association but we do not believe that crystallites are responsible for the association of EPDM. This opinion is based on the following argument.

We found that 3% solutions of sample A (with the lowest content of propylene units) form gels neither in benzene at 30° nor in toluene at 25°. In benzene, a noncoherent gel appears c 10° and a large amount of benzene is exuded. In toluene, the temperature must be well below 0° for a gel to be obtained. In this case, the gel is opaque and coherent with a small amount of solvent exuded. In both solvents, gels disappear before the temperature of measurement (i.e. 30° and 25°) is reached. The difference in behaviour for benzene and toluene can be explained by phase separation which probably occurs in the poor solvent, i.e. benzene.

From this simple experiment, we can suppose that at least most of the crystallites melt below 25°. A similar conclusion can be reached from a DSC experiment which shows that sample A melts c 35°. The dilution will decrease the melting point by 10–15°, as estimated from the crystallization theory [8].

Furthermore, crystallites would be relatively stable junctions and, in the relatively narrow concentration range used, their concentration would not change very much. Hence, their presence would influence $[\eta]$ more than k_H . With increasing temperature, such crystallite junctions must be supposed to disappear rather abruptly. The temperature dependence of $[\eta]$ for sample A is, however, smooth in both benzene and toluene. The dependence of Δk_H on temperature is also smooth and Δk_H diminishes with temperature (Figs 3 and 4).

Let us summarize. Molecules of EPDM associate in solution over a temperature range where the presence of crystallites cannot be supposed. The extent of association decreases with decreasing content of ethylene units and with increasing temperature. These conclusions are valid for both good and poor solvents. The influence of solvent cannot be specified in more detail since relatively good agree-

ment between Δk_H values in benzene and toluene does not necessarily mean the same association behaviour.

We have characterized our samples by the mole fraction of propylene units, x_p , estimated by NMR, but it is the content of ethylene units which seems to be responsible for the effect observed. Due to the presence of diene units, $(1 - x_p)$ is not equal to the fraction of ethylene units. Thus, we should expect some differences between EPM and EPDM, or between EPDM samples with different contents of diene units. Yet, the effect of diene units could be more complicated: they could change not only the stoichiometry but also the sequence distribution, and the average polymer solvent interaction. With our EPDM samples these effects do not appear to be significant.

In our considerations, we neglected the influence of association on A_2 and the effect of temperature on $[\eta]_0$. This treatment however, can only diminish the Δk_H values, so that our conclusions are still valid.

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