

Sol-Gel Analysis of the Course of Ethylene-Propylene Copolymer Cross-Linking

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A modification of the *Charlesby—Pinner* relationship is presented for the more general case of polymers with an arbitrary degree of polydispersity. The equation obtained has been applied to ethylene-propylene copolymer in which the process of cross-linking is to a considerable extent associated with chain degradation.

In the preceding paper [1], the course of polyethylene cross-linking has been investigated on the basis of the data of its sol-fraction using the *Charlesby—Pinner* relationship modified for the case of polymers with arbitrary polydispersity. From the point of view of a more general formulation of this relationship even for polymers with a degree of polydispersity exceeding 2, polyethylene still represents a relatively simple case since its cross-linking is not accompanied by a competitive degradation process.

In this study, an attempt has, therefore, been made to analyse quantitatively the course of cross-linking also for such a polyolefin, where this process is accompanied by chain degradation. For this purpose, the ethylene-propylene copolymer has been chosen as a polymer object while cumyl peroxide has been used as an initiator of the transformation reaction.

Experimental

The ethylene-propylene copolymer was a commercial product of the Montecatini's Dutral N/C type, with the molar ratio ethylene to propylene as 1—1.25 : 1 (according to the manufacturer). Its limiting viscosity number, determined in toluene at 25°C, was 146 ml g⁻¹ its density being 0.87 g cm⁻³. Before use, the polymer was purified by 24 hours extraction in boiling acetone and dried for 48 hours at 40°C and 10 Torr.

Cumyl peroxide (Perkadox SB — product of Noury et Van der Lande) was purified by threefold recrystallization in undercooled ethanol.

The polymer samples containing peroxide were prepared by mixing benzene solutions containing the required amount of the appropriate component. After evaporation of the solvent at room temperature, the samples were dried at 40°C to constant weight. Thereafter, they were sealed by common technique [2] in glass tubes in nitrogen atmosphere and kept in an air thermostat at 145 ± 0.2°C for 8 hours.

In order to remove the decomposition products of peroxide the cross-linked polymer was extracted again by using the same procedure as described above for its initial purification. The sol-fraction of the samples thus treated and containing only the polymer component was determined from the loss of weight after 28 days extraction of the polymer in benzene at room temperature. At this time, the weight already remained constant. Then the residue was dried at 60°C and 10 Torr to constant weight.

Results and Discussion

The results obtained by the above procedure, expressed by the sol-fraction of the cross-linked ethylene-propylene copolymer as a function of the peroxide concentration, are presented in Fig. 1.

Since for ethylene copolymers the ratio of the weight-average molecular weight to its number-average is generally greater than two [3], the relationship between the degree of cross-linking of this polymer and its sol-fraction (s) cannot be expressed by the simple relation

$$\gamma = (s + s^{0.5})^{-1} \quad (1)$$

suitable only for polymers with most probable molecular weight distribution [4]. As already formerly stated [1], the form of equation (1) is only a solution for the simpler and more frequent case of polymers with the degree of polydispersity equal to two. It is, however, deduced from the relation

$$\gamma = \frac{s^{\frac{1}{R}-1} - 1}{1 - s} (R - 1)^{-1} \quad (2)$$

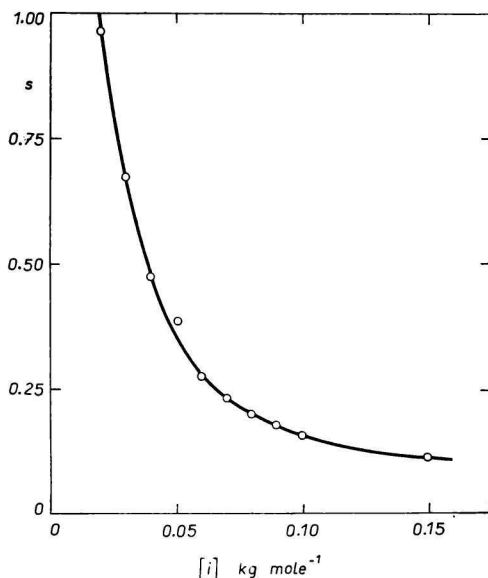


Fig. 1. The decrease of the sol-fraction of ethylene-propylene copolymer (s) as a function of cumyl peroxide concentration ($[i]$), determined after 8 hours cross-linking at 145°C.

with more general validity for polymers with arbitrary degree of polydispersity (R).

Since the analysed copolymer degrades simultaneously with its cross-linking, its degree of cross-linking (defined as the number-average of cross-links per one macromolecule with the number-average molecular weight \bar{M}_n after its simultaneous degradation) changes (decreases) in the course of the reaction in contrast to polyethylene. The change of γ for this kind of polymer transformation may be expressed, however, by the degree of cross-linking with respect even to the original chain (γ_0) by using the ratio between the rate of degradation and that of cross-linking (q/p) according to the expression [5]

$$\gamma = \frac{\gamma_0}{1 + \frac{q}{p} \gamma_0}. \quad (3)$$

After rearrangement, equation (2) can be expressed as

$$\frac{1-s}{s^{\frac{1}{R}-1} - 1} = \left[\gamma_0(R-1) \right]^{-1} + \left[\frac{p}{q} (R-1) \right]^{-1}. \quad (4)$$

Here, γ_0 is related to a polymer in which the degradation process does not occur, so that its value may be replaced by the expression

$$\gamma_0 = 2 \times 10^{-3} \bar{M}_n p [i]. \quad (5)$$

This relation has been deduced previously for the analysis of the course of polyethylene cross-linking [1]. Thus the relation (4) obtains the final form

$$\frac{1-s}{s^{\frac{1}{R}-1} - 1} = \frac{5 \times 10^2}{p \bar{M}_n} (R-1)^{-1} [i]^{-1} + \frac{q}{p} (R-1)^{-1} \quad (6)$$

expressing the sol-fraction of the polymer as a function of the peroxide concentration ($[i]$). The plot of (6) is a straight line the slope and intercept of which being

$$\frac{5 \times 10^2}{p \bar{M}_n} (R-1)^{-1} \quad \text{and} \quad \frac{q}{p} (R-1)^{-1}, \text{ resp.}$$

For the evaluation of the results (Fig. 1) obtained from the relation (6), it is necessary also to know the constant R . As this constant expresses the degree of copolymer polydispersity, its value might be obtained from the ratio between the weight-average and number-average molecular weight (\bar{M}_w/\bar{M}_n). But the attempt to determine the weight-average molecular weight by the method of light scattering was not successful because the analysed copolymer formed a microgel in solution. For this reason, another indirect method had to be applied for the determination of the constant R , involving the following procedure. According to the given definition of R , the slope of equation (6) may be expressed as follows:

$$K = \frac{5 \times 10^2}{p \bar{M}_w} \left(1 - \frac{1}{R} \right)^{-1}.$$

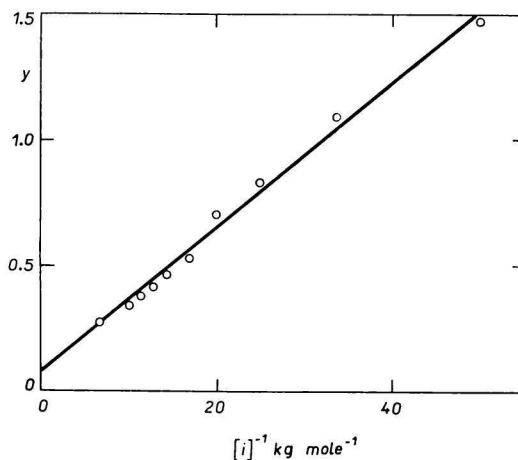


Fig. 2. Plot of equation (6) for the experimental values of Fig. 1 for $R = 3$.
 y and $[i]^{-1}$ denote the value of the fraction

$$\frac{1-s}{s^{\frac{1}{3}}-1}$$

and the reciprocal value of cumyl peroxide concentration, respectively.

Since the peroxide concentration, characteristic for the beginning of gel formation ($[i]_g$), is for polymers with different polydispersities but equal weight-average molecular weights always the same [6], the solution of equation (6) gives on performing the above slope transformation and substituting $R = \infty$ for the gel point ($s = 1$)

$$[i]_g = \frac{5 \times 10^2}{p\bar{M}_w}. \quad (7)$$

According to the course of copolymer cross-linking (Fig. 1), the gel formation sets in at the peroxide concentration of $[i]_g = 1.9 \pm 0.2 \times 10^{-2}$ mole kg^{-1} (extrapolation refined by calculation) so that the slope of equation (6) shall have the value of $1.9 \times 10^{-2} (1 - 1/R)^{-1}$ mole kg^{-1} . For the experimental results given in Fig. 1, this condition is best fulfilled by such a solution of equation (6) for which $R = 3 \pm 0.2$. This solution implies that the value of the slope is 2.85×10^{-2} mole kg^{-1} . (This result was obtained by repeated approximation, in which the values of the slope in (6) were calculated by the least-square method using arbitrarily chosen values of R .) The most satisfactory solution thus achieved is illustrated in Fig. 2. The value of q/p is found to be 0.15 indicating a relatively important part of the degradation during the cross-linking of the ethylene-propylene copolymer. Similar result has been found by the use of another method, too [7].

The linear dependence of the sol-fraction of ethylene-propylene copolymer with varying amounts of peroxide, during the cross-linking reaction makes possible to estimate the extent of the degradation of the polymer, as well as the concentration of the cross-links formed.

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