Bulk Functionalization of Ethylene–Propylene Copolymers. II. Influence of the Initiator Concentration and of the Copolymer Composition and Chain Microstructure on the Reaction Kinetics

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Synopsis

The effect of the dicumylperoxide (DCPO) concentration on the kinetics of the bulk functionalization of an ethylene–propylene copolymer (EPR) has been studied. It has been found that, enhancing the DCPO initial concentration in the reaction mixture, results in both increased initial reaction rate and grafting process efficiency. DCPO content also affects degradation, which always accompanies the grafting reaction. At high DCPO content, products with a high degree of grafting and intrinsic viscosity close to that of the parent copolymer can be obtained. Furthermore, the influence of the EPR composition and chain microstructure on the functionalization as well as on the degradation processes has been investigated. By increasing the C_2 content in EPRs prepared by using vanadium-based conventional catalysts, obtains faster functionalization kinetics and a less pronounced degradation of the products. At fixed experimental conditions, the highest grafting degrees have been obtained by using EPRs prepared by high-yield titanium catalysts and characterized as a block-like microstructure. The experimental results have been interpreted on the basis of a proposed reaction mechanism.

INTRODUCTION

Polyolefin modification by grafting unsaturated polar groups onto the polymer backbone has been widely investigated.[1-6] The increased polarity which can be achieved in this way can improve some physicomechanical properties of the modified polyolefins, such as adhesion to other materials (e.g., metal or glass), and can promote better compatibility with other polymers. A number of articles have been issued on the functionalization reaction carried out in solvent media and initiated by means of organic peroxides.[3-7] By this route several unsaturated polar groups were grafted, such as maleic anhydride (MAH) and maleic acid, maleic and fumaric esters.[7] An ethylene–propylene copolymer (EPR) grafted with this highly reactive MAH was successfully used as a toughening agent of polyamide-6.[8-11]

A systematic investigation on the bulk functionalization of EPR was undertaken by the authors.[12-14] Dibutyl maleate (DBM) was selected to be

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grafted onto the EPR chains on the basis of its low volatility, and, especially, its compatibility with the polymeric substrate.[13] Dicumylperoxide (DCPO) was chosen as radical initiator because of its decomposition rate in the explored temperature range.

In the first article of this series,[13] a processing procedure consisting of premixing the reactants at 90°C (temperature at which no DCPO decomposes) and of successive reaction, was developed. The conceptual importance of separating these two main steps of the process, provided that the components are mixable, was recognized and discussed. Moreover, the effect of temperature and of two different processing procedures on the kinetics of the bulk EPR functionalization was studied. The complex reaction mechanism through which the functionalization occurs, was also discussed.

In the present work the effect of the initial DCPO concentration on the kinetics of the grafting reaction as well as on its efficiency, has been analyzed. Moreover, on the basis of the proposed molecular mechanism, the relevance of EPR composition and chain microstructure on both the kinetics and the efficiency of the process has been recognized and studied. Further details on the reaction mechanism governing the functionalization process have been obtained from the experimental results.

In a subsequent article,[14] the results of a structural and superstructural investigation on functionalized EPRs having different degrees of grafting will be reported.

EXPERIMENTAL

Materials

The ethylene-propylene copolymers used in this study (kindly supplied by Dutral S.p.A., Ferrara, Italy) are reported in Table I. The dibutylmaleate was reagent grade. The dicumylperoxide was crystallized from absolute ethanol and stored under vacuum with P_2O_5. Acetone was reagent grade and used without further purification.

Premixing of Reactants

EPR 45.0 g was introduced in the mixing chamber of a Brabender-like apparatus (Rheocord EC, Haake Inc., Saddle Brook, NJ) at 90°C. After

TABLE I
Characterization Data of Ethylene–Propylene Copolymers

Trade name	Wt % of C_3[a]	Catalytic system	$[\eta]$[b] (dL/g)
Co054	44	V	2.0
Co034	28	V	2.0
DAR 67/17	45	Ti	1.7
DAR 58/3	28.5	Ti	2.1

[a] Determined by IR spectroscopy.

[b] In tetrahydronaphthalene at 135°C.

Abbreviations: V = conventional vanadium-based catalytic system, Ti = high-yield titanium-based catalytic system.

TABLE II
Composition of the Reaction Mixtures before and after the Premixing Step

Code	Feed composition by wt EPR/DBM/DCPO	Real composition by wt EPR/DBM/DCPO
A	100/10/0.5	100/8.1/0.4
B	100/10/0.7	100/8.2/0.6
C	100/10/1.0	100/8.2/0.8
D	100/10/1.5	100/8.2/1.2
E	100/10/2.0	100/8.2/1.6

Abbreviations: EPR = ethylene–propylene rubber, DBM = dibutyl maleate, DCPO = dicumyl-peroxide.

temperature stabilization, a solution consisting of 4.50 g of DBM and different amounts of DCPO was added and the mixture was mixed for a further 5 min at a roller speed of 32 rpm. Five different reaction mixtures were investigated in the case of the Co-054 copolymer. The real compositions of the reaction mixtures after the premixing step were determined using gravimetric and spectroscopic methods (infrared, [1]H-nuclear magnetic resonance) as described in Ref. 13, and reported in Table II.

Reaction Procedure

After the premixing step, 0.5 g of the reaction mixture was introduced in a glass tube immersed in a thermostatted bath kept at 150°C. After the desired time, the reaction was stopped by quenching the sample with cold acetone.

Product Analysis

At the end of the reaction, the product (in the form of films of 0.15 mm thickness) was freed from unreacted DBM and other secondary products, in acetone at room temperature. After 12 h, the purification procedure was verified as complete.

Evaluation of the grafting degree of EPR-g-dibutylsuccinate, (EPR-g-DBS) samples was performed by dissolving 0.100 g of mixture in 10 mL of carbon tetrachloride. The 1738 cm^{-1} C$=$O stretching absorption of the grafted ester groups was used as an analytical band. From a calibration curve obtained from a series of solutions of known concentration of dibutylsuccinate (DBS) in CCl$_4$, the amount of grafted DBS onto the copolymer backbone was estimated. The above determination is not reliable for the lowest values of grafting degree because of the weak intensity of the 1738 cm^{-1} band. In these cases, the IR analysis was performed on thin films ($\sim$ 0.1 mm) of the reaction products using the molar absorptivity value of free DBS in nonpolar solvents (0.468 mm/mL mg^{-1}).

The film thickness was determined using the band at 4330 cm^{-1}.[15,16] For intermediate values of grafting degree both methods can be applied and the results are coincident within experimental errors.

The [η] values were measured with a Cannon-Ubbelhode viscosimeter at 135°C using concentrations from 0.200 to 1.00 g/dL of product in freshly distilled tetrahydronaphthalene.

RESULTS AND DISCUSSION

Effect of DCPO Concentration

In the first article of this series,[13] the influence of the reaction temperature and of the type of processing on the functionalization kinetics of an EPR having 44% by weight of C_3 (Co054 of Table I) was studied.

Another parameter which plays a fundamental role in determining the overall kinetic behavior of the process is the composition of the reaction mixture. In particular, in the present work, the effect of the radical initiator concentration on the initial reaction rate and on the total efficiency of the process was investigated.

The molecular mechanism for the bulk EPR grafting, which has already been proposed and discussed in detail,[12,13] is summarized in the Scheme I, in which PH is the polymeric substrate, R· is a primary radical generated by the DCPO decomposition, and M is DBM.

The reaction was carried out at 150°C on reactant mixtures, premixed at 90°C in a Brabender-like apparatus, according to the static method previously reported.[13] The half-life of DCPO at 150°C is 17 min in dodecane.

In Figure 1 the values of the grafting degree (reported as mmol of grafted DBM per 100 g of product) are plotted as a function of the reaction time for five feed compositions of the reaction mixture differing for the initial DCPO concentration. (The nominal EPR/DBM ratio is in all cases 100/10 w/w, while the nominal DCPO content ranges from 0.5 up to 2.0 w/w). The real compositions, used in all the successive calculations, differ from the nominal ones because of some leakages. They were directly measured after the premixing step, as described in the Experimental section.
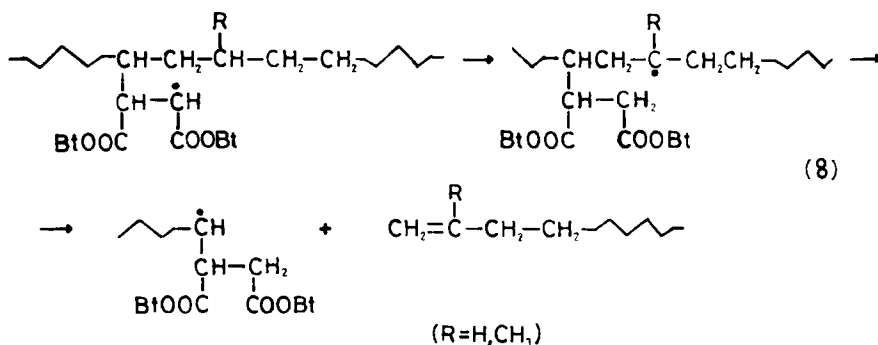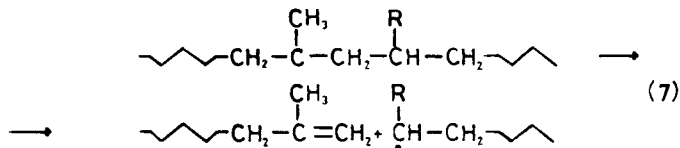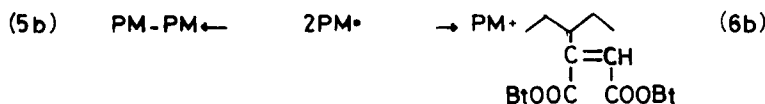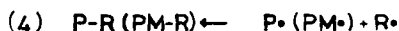
After an initial linear trend, all the curves in Figure 1, reach a plateau. An induction period is observed in all the cases. Its length decreases going from the A to B composition while it is almost constant for the three remaining compositions. The slopes of the linear portion of the curves as well as the values of the grafting degree relative to the plateau regions increase by enhancing the DCPO content. From these slopes the initial reaction rates R_i have been evaluated. A linear relationship has been obtained between R_i and the one-half power of the DCPO initial concentration as shown in Figure 2. This indicates a reaction order of one-half with respect to the radical initiator concentration.

In Figure 3 (curve A) the values of the grafting degree relative to the plateau regions have been plotted as a function of the DCPO initial concentration. As expected, increasing concentrations of DCPO enhance the grafting degree and for B, C, D, and E compositions a linear relationship holds.

The effect of DCPO concentration on the final values of grafting degree can be better discussed by considering the radical initiator efficiency φ defined as:

$$\varphi = \frac{[DBM]_g}{2[DCPO]_o}$$

where $[DBM]_g$ and $[DCPO]_o$ are the concentrations of reacted DBM and of DCPO initially present in the mixture, respectively (curve B in Fig. 3).

$$\text{Per} \rightarrow 2R\cdot$$

$$PH + R\cdot \rightarrow P\cdot + RH \qquad (1a)$$

$$P\cdot + M \rightarrow PM\cdot \qquad (1b)$$

$$PM\cdot + M \rightarrow PMM\cdot \qquad (2)$$

$$PM\cdot + PH \rightarrow PMH + P\cdot \qquad (3)$$

$(4) \quad P-R\,(PM-R) \leftarrow \quad P\cdot\,(PM\cdot) + R\cdot$

$(5a) \quad\quad P-P \leftarrow \quad 2P\cdot \quad \rightarrow PH + \text{/\\/\\}\quad (6a)$

$(5b) \quad PM-PM \leftarrow \quad 2PM\cdot \quad \rightarrow PM + \text{/\\/\\}\quad (6b)$

$$\underset{\text{BtOOC\quad COOBt}}{\overset{C=CH}{}}$$

$(5c) \quad\quad P-MP \leftarrow \quad P\cdot + PM\cdot \quad \rightarrow PM + \text{/\\/\\}\quad (6c)$

$$(7)$$

$$(8)$$

$$(R = H, CH_3)$$

Scheme 1.

This parameter indicates the number of grafted DBM molecules per primary radical $R\cdot$ produced in the system and can give valuable information on the molecular mechanism governing the process.

A first observation is that φ is in all cases greater than one. This would indicate that reactions such as (2) and/or (3) of Scheme I, which enhance the efficiency by yielding products (PM) and regenerating, at the same time, macroradical species such as $P\cdot$ and $PM\cdot$ are highly active in the system. Reaction (2) (DBM homopolymerization) cannot be considered likely to occur as DBM is a bulky 1,2-disubstituted olefin. We have also checked that DBM homopolymerization does not occur in experimental conditions similar to those of the grafting process. It must be concluded that the chain transfer mechanism of type (3) plays an important role in the overall grafting process.
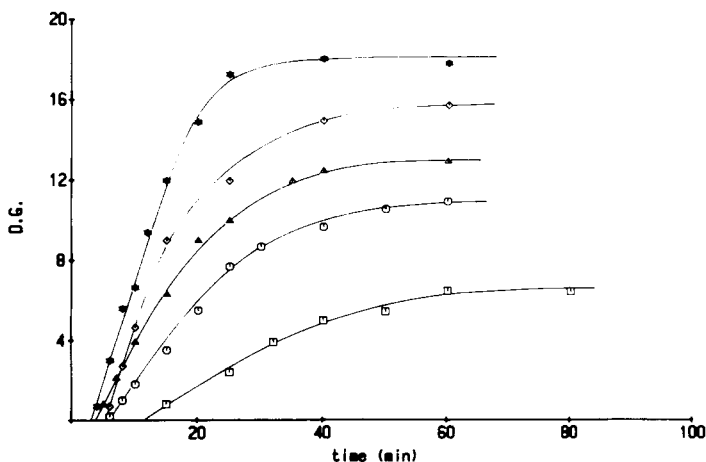
Fig. 1. Influence of the DCPO concentration on the reaction kinetics; □, ○, △, ◇, * corresponding to reaction mixtures A, B, C, D, and E of Table I, respectively. The grafting degree is expressed as mmol of grafted DBM per 100 g of product.

For compositions B, C, D, and E, a gradual decrease of φ by enhancing the DCPO initial concentration was found. This effect can be ascribed to the higher peroxide concentrations that produce higher concentrations of primary radicals and consequently of macroradicals in the system. Hence secondary reactions of coupling and/or of disproportionation among these species, such as (5a), (5b), (5c), and/or (6a), (6b), (6c), which consume the active sites, can occur to a larger extent.

In the case of A composition, the values of φ and of the grafting degree at the end of reaction are significantly lower than expected on the basis of the above considerations. This effect could be related to the presence, in the kinetic curve relative to this composition, of a long induction period
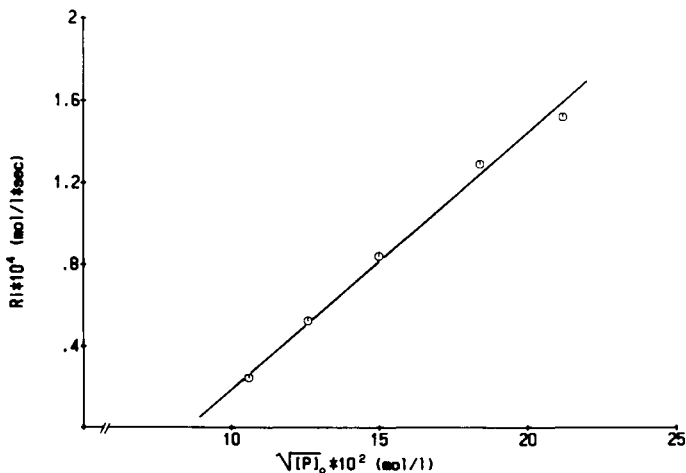

Fig. 2. Dependence of the initial reaction rate, R_i, on the square root of the initial concentration of DCPO, $[P]_o$.
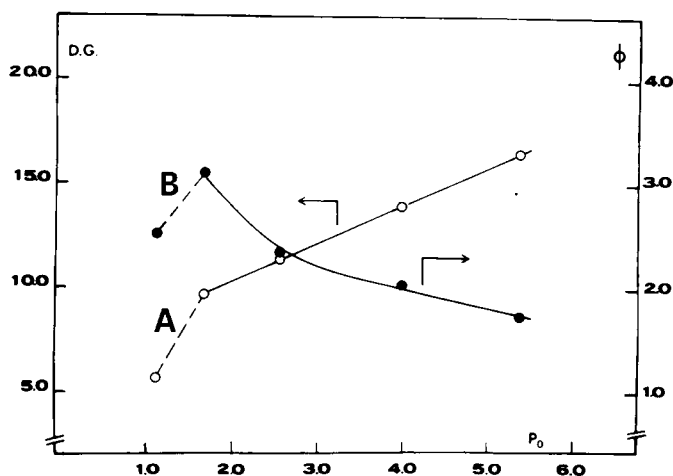
Fig. 3.   Influence of the DCPO initial concentration, P_o, on the maximum grafting degree, D.G. (curve A), and on the radical initiator efficiency, φ, (curve B). P_o and D.G. are expressed as mmol per 100 g of product.

(10.5 min). During this period a large number of macroradicals can be consumed by a parasitic cage mechanism previously proposed,[13] thus producing a considerable decrease in reaction efficiency.

It has been observed[4,5,12,13] that the grafting process is accompanied by a complex rearrangement of the molecular characteristics of the copolymer substrate, due to the occurrence of reaction steps such as (5a), (5b), (5c), and (7), (8) which affect the molecular structure of the EPR. These complex phenomena have been qualitatively monitored by measuring the intrinsic viscosities of the reaction products as a function of time. The results of such an analysis have been reported in Figure 4. A decrease in $[\eta]$ values with reaction time is observed for A, B, C, and D compositions, thus indicating that
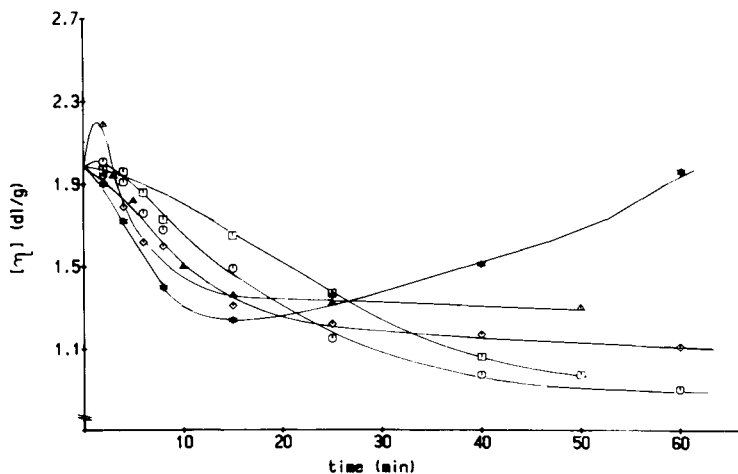

Fig. 4.   Dependence of the intrinsic viscosity of the products on the reaction time; □, ○, △, ◇, *, correspond to the reaction mixtures A, B, C, D, and E of Table I, respectively.

in these cases chain scission reactions of type (7) and (8) strongly prevail over coupling reactions (5a), (5b), (5c).

This behavior is in agreement with that previously observed for the C composition under different experimental conditions.[13] The curve relative to the composition E presents a different shape for high reaction times and will be discussed later.

The considerable degradation of the polymeric substrate for four of the five investigated compositions can be explained as follows:

Both secondary and tertiary macroradicals are formed by hydrogen abstraction on the polymeric chains promoted by primary R· radicals. Their relative amount depends on their stability (tertiary > secondary) and population (secondary > tertiary). In the absence of DBM, secondary macroradicals preferentially undergo crosslinking reactions while tertiary macroradicals lead to β-scission processes.[17,18] The crosslinking efficiency of organic peroxides is much higher in polyethylene than in polypropylene.[19] In the case of EPR, even if both mechanisms are active, the coupling prevails over β-scission as evidenced by the finding of a considerable amount of gel fraction in the reaction products.[13]

When DBM is present, the grafting occurs together with the above reactions, but, assuming that it involves the secondary macroradicals more easily than the tertiary ones, the balance between coupling and β-scission is shifted toward the latter. This assumption, which is reasonable because of the steric hindrance exerted by the methyl group on the approaching DBM molecule, is supported by a structural and superstructural investigation carried out on functionalized EPRs having different degrees of grafting.[14] In conclusion, the grafting successfully competes with the coupling thus favoring the β-scission processes.

For the composition E, having the highest DCPO concentration, an anomalous behavior was observed. In fact, after an initial steep decrease, the $[\eta]$ values begin to rise, gradually approaching the initial $[\eta]$ value of the parent polymer. From Figures 1 and 4, it can be observed that when the $[\eta]$ value starts to increase, most of the grafting reaction has already occurred, lowering the concentration of free DBM in the system. At the same time, the actual macroradical concentration is still high because of the high initial DCPO content (2 parts by wt) and because of its low decomposition rate at 150°C. Thus the system evolves, as in the absence of DBM, toward the polymeric substrate crosslinking and the products obtained at the end of the reaction $(t_r > 80')$, have $[\eta]$ values comparable to that of the parent EPR. Nevertheless their molecular characteristics, because of a high degree of branching, are likely to be quite different from those of the ungrafted polymer.

Effect of EPR Composition and Microstructure

The assumption that the grafting reaction preferentially involves the secondary macroradicals while the tertiary ones are responsible for the β-scission processes suggests that both the composition and the microstructure of the EPR may affect the grafting degree and the chain degradation of reaction products obtained under the same experimental conditions. Therefore, two series of copolymers were investigated, the first obtained using vanadium-based

conventional catalytic systems, the second obtained by using new high-yield titanium-based catalytic systems.[20] The copolymers have similar molecular weights (see Table I) and different chain microstructure. V-EPRs have low values of the product of reactivity ratios ($r_1 \cdot r_2 < 1$) and have a significant amount of enchainment inversions for C_3 units, that is, head-to-head placement of successive propylene units (about 10%), while Ti-EPRs have a block-like character ($r_1 \cdot r_2 > 2$) and are practically free from inversions.[20] For both series, two compositions were examined: 28% and 44–45% by weight of C_3, in which the reaction temperature (150°C) and the composition of the reaction mixture (100/10/1 EPR/DBM/DCPO) were kept constant. The effect of EPR composition on the kinetics of grafting is shown in Figure 5 for V-EPRs. Both the initial reaction rate and the maximum grafting degree are higher for the copolymer having higher amount of C_2 units.

No such effect was detected in the case of Ti-EPRs, as copolymers of different composition exhibit quite similar kinetic behavior. Both Ti-EPRs show, in fact, fast grafting kinetics reaching high grafting degree values in the plateau region. A comparison between Ti-EPR and V-EPR, both having 44% by wt of C_3, is presented in Figure 6. It is worth noting that the effect of the microstructure on the grafting reaction is greater than that of composition as the amount of grafted DBM is always higher in the case of 44% C_3 Ti-EPR than in the case of 28% C_2 V-EPR at a given reaction time (compare Figures 5 and 6).

The influence of the copolymer composition on the chain degradation is shown in Figure 7, where the intrinsic viscosity is plotted against the reaction time. In the case of copolymers of higher C_3 content, lower viscosity values are found for both Ti and V-EPRs. In particular, comparing the kinetic and degradation behavior of V-EPRs, the copolymer which presents higher grafting degrees (28% by wt of C_3), shows less pronounced degradation phenomena. This result is remarkable as we have found in this and in previous work[12,13] that, by changing parameters such as reaction temperature and peroxide
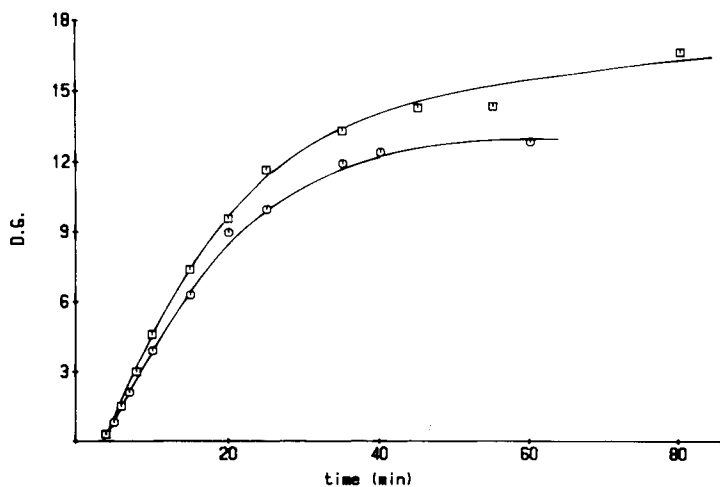

Fig. 5.   Influence of the V-EPR composition on the reaction kinetics; O = 44% of C_3 by wt (Co054), □ = 28% of C_3 by wt (Co034).
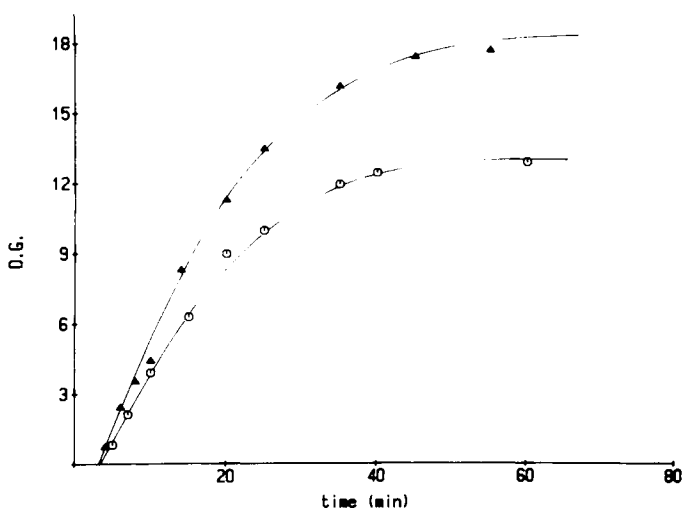
Fig. 6. Influence of the chain microstructure on the reaction kinetics; O = V-EPR of 44% by wt of C_3 (Co054), △ = Ti-EPR of 45% by wt of C_3 (DAR 67/17).
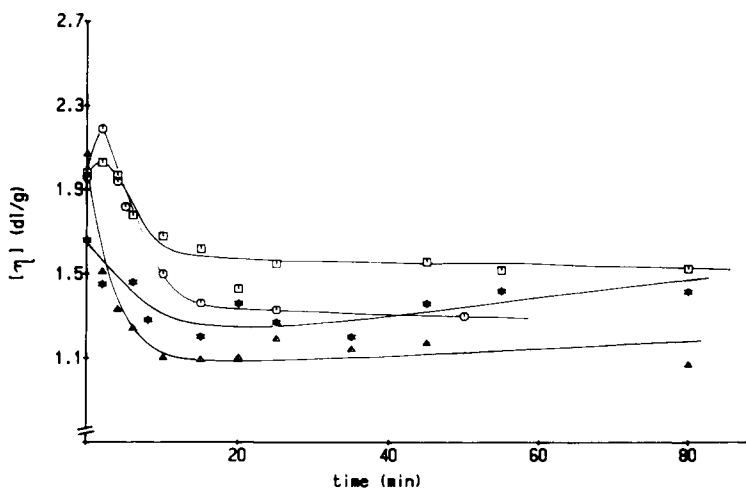

Fig. 7. Dependence of the intrinsic viscosity of the products on the reaction time for copolymers having different compositions and chain microstructures; △ = DAR 67/17, * = DAR 58/3, O = Co054, □ = Co034.

concentration, the higher the grafting degree the higher the extent of chain degradation. Moreover comparison of the viscosity data in Figure 7 for 44% C_3 Ti- and V-EPRs shows a more pronounced degradation in the case of the former copolymer.

The experimental results obtained by varying the copolymer composition and microstructure may be rationalized on the following bases:

1. The grafting preferentially occurs on secondary macroradicals and the reaction rate and the maximum attainable grafting degree are both enhanced with increasing the ethylene content in the EPR.

2. Secondary macroradicals in which the active sites belong to methylene sequences are more reactive toward the DBM addition, the block-like character of Ti-EPR thus favoring the functionalization reaction.

3. In the Ti-EPRs the high efficiency of the grafting reaction likely masks the effect of composition, as long $-CH_2-$ sequences are present also in the Ti-EPR of low C_2 content because of its chain microstructure.

4. The frequency of the β-scission reactions which involve tertiary macroradicals is reduced with increasing C_2 content. In the copolymers having the same composition, 44% C_3, the Ti-EPR is degraded faster and to a larger extent. This finding may be related to the higher grafting degrees achieved by this copolymer since the grafting may induce further β-scission through the reaction mechanism (8).

Points (1) and (2) are reasonably explained on the basis of steric effects, that is the bulky DBM molecules preferentially add to less hindered secondary macroradicals especially if they are far removed from C_3 units, as in longer methylene sequences.

Furthermore, for point (2), structural and superstructural investigations on functionalized EPRs[14] having different amounts of grafted DBM support the view that long C_2 sequences are strongly involved in grafting reactions.

CONCLUSIONS

In the bulk functionalization of EPRs it is highly desirable to reach high levels of grafting with a reduced amount of chain degradation.

By varying temperature and processing conditions, as shown previously, the higher the grafting degree the higher the viscosity drop for the reaction products. Using proper peroxide concentration, high functionalization levels with viscosity values close to that of the parent EPR have been obtained. As expected on the basis of the proposed reaction mechanism, the nature of the EPR affects the grafting degree and the molecular characteristics of the resulting functionalized EPRs.

In the case of V-EPRs, higher C_2 contents are required to obtain high grafting degree without extensive chain degradation. The highest grafting degrees for a given composition can be reached by using elastomers prepared by high-yield titanium catalytic systems and characterized by a block-like microstructure.

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