Bulk Functionalization of Ethylene–Propylene Copolymers. III. Structural and Superreticular Order Investigations

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Synopsis

An ethylene–propylene copolymer (EPR) has been functionalized with dibutyl maleate (DBM) by means of a radical-initiated bulk process. Different degrees of grafting have been obtained by varying the overall composition of the reaction mixture as well as the processing procedures. The influence of the grafting degree on the structural and superreticular (or "long range") order has been investigated by differential scanning calorimetry (DSC), Fourier transform infrared analysis (FTIR), and wide (WAXS) and small angle X-ray scattering (SAXS) techniques. The functionalization leads to a decrease of the "residual crystallinity" present in the parent copolymer. Linear relationships between the grafting degree and the crystallinity degree X_c evaluated by both DSC and WAXS have been obtained. The results of the structural investigations, in agreement with previously reported ones, suggest that the grafting preferentially occurs onto the longer or more perfect methylene sequences. SAXS investigations showed that the significant degree of structuration, i.e., crystalline and paracrystalline order, present in the parent elastomer, gradually disappears by increasing the degree of grafting.

INTRODUCTION

Ethylene–propylene rubbers (EPRs) have been modified by attaching polar groups such as anhydride and esters onto the copolymer backbone[1-5] in order to improve some properties (adhesion, dyeability) or to perform successive reactions such as crosslinking or grafting. The functionalization process has been performed either in solution or in bulk by grafting unsaturated molecules bearing the functional group. Organic peroxides have been used as radical initiators. We have particularly investigated the bulk modification of EPRs, selecting dicumylperoxide (DCPO) as radical initiator and dibutyl maleate (DBM).[3-5] Varying the reaction temperature, processing conditions, composition of the reaction mixture, and composition and chain microstructure of the EPR copolymer, it is possible to obtain different amounts of grafted functional groups. During the grafting reaction, the EPRs also undergo a complex rearrangement of their molecular characteristics. Reaction mechanisms have been proposed and discussed in detail.[3-5]

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A structural and superstructural characterization of the modified EPRs appears to be interesting in order to evaluate their potential end uses and may also yield additional useful information to better understand the complex reaction patterns occurring in the modification process. In the present work we report the results of an IR, differential scanning calorimetry (DSC), and wide (WAXS) and small angle X-ray scattering (SAXS) investigation on an EPR copolymer, having 28%wt C_3, modified by grafting different amounts of DBM by means of a bulk process. The main aim of this study was to elucidate the influence of the grafting degree on the structural and superreticular order of the modified EPRs.

EXPERIMENTAL

Materials

The EPR used, kindly supplied by Dutral Company (Ferrara, Italy), was Dutral Co034 an ethylene–propylene copolymer 28%wt C_3, having an intrinsic viscosity of 1.95 dL/g in tetrahydronaphthalene at 135°C. The dibutytl maleate was reagent grade. The dicumylperoxide was recrystallized from absolute ethanol and stored under vacuum with P_2O_5.

Grafting reaction

The grafting reactions were carried out in a Brabender-like apparatus (Rheocord EC, Haake Inc., Saddle Brook, NJ) at 32 rpm. The standard two-step dynamic procedure described in detail in previous papers[3,4] has been used to prepare the low grafting degree products (Procedure A). The reactants (EPR, DBM, and DCPO) were premixed at 90°C. After this step, the temperature was raised to 160°C and mixing was continued for 30 min. High peroxide concentrations are required to reach high grafting degrees;[5] as these experimental conditions led also to extensive crosslinking of the reaction products, an alternative method was developed (Procedure B). In this procedure, the DBM/DCPO solution was added to the molten copolymer at 160°C in three equal portions at 15 min intervals. After the last addition, mixing was continued for an additional 15 min. Using this method, products completely soluble in xylene at room temperature were obtained. The grafting degree (GD) was varied by changing the overall composition of the reaction mixture. The purification and the characterization of the products were performed according to the methods reported in previous articles.[4-6] The purification procedure completely removes ungrafted DBM. The results obtained on the functionalized copolymers have been summarized in Table I, together with the characterization data of the parent EPR.

Techniques

Thermal analysis was performed on 15 mg of sample by using a Mettler TA-3000 differential scanning calorimeter. The scanning rate was 20°C/min. The temperature and enthalpy calibrations were done using indium as standard.

TABLE I
Preparation and Characterization of the Investigated Copolymers[a]

Copolymer code	Composition of the reaction mixture (EPR/DBM/DCPO by wt)	Reaction procedure[b]	Grafting degree of DBM (%wt)	$[\eta]$ (dL/g)
EPR-0	—	—	0	2.0
EPR-3.7	100/10/1	A	3.7	1.6
EPR-5.1	100/20/2	A	5.1	1.5
EPR-10	100/30/3	B	10.0	1.3
EPR-13	100/40/4	B	13.4	—

[a] EPR = ethylene–propylene rubber, DBM = dibutyl maleate, DCPO = dicumylperoxide.
[b] See text for explanation.
[c] In tetrahydronaphthalene at 135°C.

Infrared measurements were performed on thin films (ca. 0.1 mm) using a Nicolet DX-5B Fourier transform infrared spectrophotometer. The film thickness was evaluated both by a suitable micrometer and by measuring the absorbance of the 4330 cm^{-1} band, as described in refs. 6 and 7. The results obtained with the two methods were the same.

Sheets of 1.5 mm thickness, obtained by compression molding at 160°C were used in the X-ray experiments.

WAXS profiles were carried out at 20 ± 0.5°C by a PW 1050/71 Philips powder differactomer (Cukα, nickel-filtered radiation) in the reflection mode, scanning 2θ angle in continuous.

SAXS profiles were collected (by means of the same radiation and at the same temperature) by a step by step automated Rigaku Denki camera with a resolving power up to about 800 Å, scanning the scattering 2θ angle at intervals of 0.01°; counting times were 1000 s/point. The intensities were corrected for parasitic scattering (background) and for absorption.

RESULTS AND DISCUSSION

Functionalized EPRs with grafting degrees ranging from 3.7 to 13.4% by weight of DBM were obtained by a bulk reaction using DCPO as radical initiator according to previously reported procedures. A modification of the standard procedure was adopted to obtain the highest grafting degrees (see Experimental). The characterization data of the modified EPRs are reported in Table I together with those of the parent copolymer.

Structural Investigations

The thermal behavior of the functionalized EPRs as well as that of the parent EPR is strongly dependent on their thermal history. Such effects are illustrated in Figure 1 where the DSC traces of an EPR-10 sample, subjected to different thermal treatments, are reported as an example. Immediately after a melting-cooling cycle only a broad melting endotherm, starting just after the glass transition step, is observed (curve A). Annealing at room temperature (25°C) brings a modification of the DSC thermogram. The broad endotherm slowly separates into a low temperature melting region and into a high temperature melting peak (peak 2), centered at 50°C, with increasing
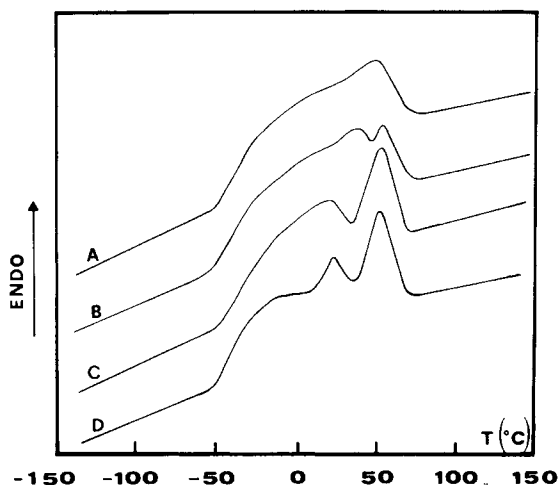
Fig. 1. DSC traces of EPR-10: (A) immediately after a melting-cooling cycle; (B) after 1 day at 25°C; (C) after 15 days at 25°C; (D) sample as (C) annealed for 10 h at 0°C.

annealing time (1 day, curve B; 15 days, curve C). No further modifications of curve C were detected by annealing at this temperature for longer times. A sharp melting endotherm, centered at 25°C (peak 1), develops also in the low temperature melting region upon annealing at 0°C for 10 h (curve D). A qualitatively similar behavior was observed for EPR-0 and for the other functionalized EPRs.

Figure 2 shows the thermograms of all the investigated EPRs obtained as in the case of curve D of Figure 1, i.e., after 15 days annealing at 25°C followed by 10 h annealing at 0°C. Some common features are observed: (1) two close melting endotherms are evident by proper thermal treatments; (2) the melting
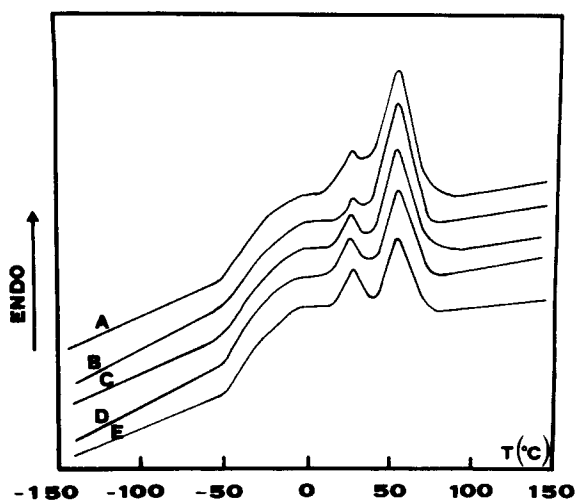

Fig. 2. DSC traces of the investigated EPRs annealed for 10 hours at 0°C: (A) EPR-0; (B) EPR-3.7; (C) EPR-5.1; (D) EPR-10; (E) EPR-13.
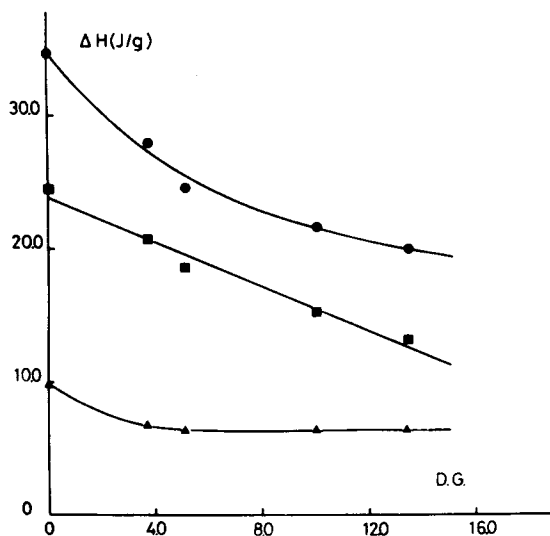
Fig. 3. Melting enthalpy, ΔH, as a function of the grafting degree GD, for the investigated elastomers; ●: overall ΔH, ■: ΔH relative to the peak at 51°C (peak 2), ▲: ΔH relative to the peak at 20°C (peak 1).

temperatures, T_{m1} and T_{m2} are practically independent of the degree of grafting.

Considering that in our system the crystallinity is of polyethylene-like type, as shown by WAXS experiments (vide infra), we may assume that the high temperature endotherm is related to the melting of a crystallizable material characterized by long methylene sequences having a low number of chain defects (C_3 units). More disordered or shorter polyethylene segments give rise to the broad low temperature endotherm which falls below room temperature; reordering and recrystallization of this material is possible only by annealing at 0°C. A comparison of the endotherm areas in Figure 2 shows that the overall area (peak 1 + peak 2) gradually decreases with increasing the degree of grafting. Moreover, the ratio (peak 1/peak 2) areas also depends on the grafting degree.

A quantitative evaluation of these effects have been attempted by performing the deconvolution of the two peaks. The results are shown in Figure 3 where the overall enthalpy of fusion, ΔH_T, and the enthalpies of fusion, ΔH_1 and ΔH_2, are plotted as a function of the grafting degree of the EPRs. ΔH_1 is practically constant for all the functionalized EPRs at a value slightly lower than that of the parent EPR, while a linear lowering of ΔH_2 with increasing the grafting degree is found. The disruption of long methylene sequences by the grafting of the bulky DBM molecules was confirmed by the analysis of the FTIR spectra of the investigated copolymers, performed on thin films immediately after compression molding at 150°C. Figure 4 shows the FTIR spectra in the 2000–600 cm^{-1} region, of EPR-0 (A) and of EPR-3.7 (B). The B spectrum shows two new strong absorptions, at 1738 cm^{-1} (ν C=O) and 1180 cm^{-1} (ν C—O—C). Finer differences may be observed in the 721 cm^{-1} band which is attributed to the rocking-mode vibration of long methylene sequences ($—(CH_2)_n—$ with $n \geq 5$).[7] A scale expansion of this band, normalized for the
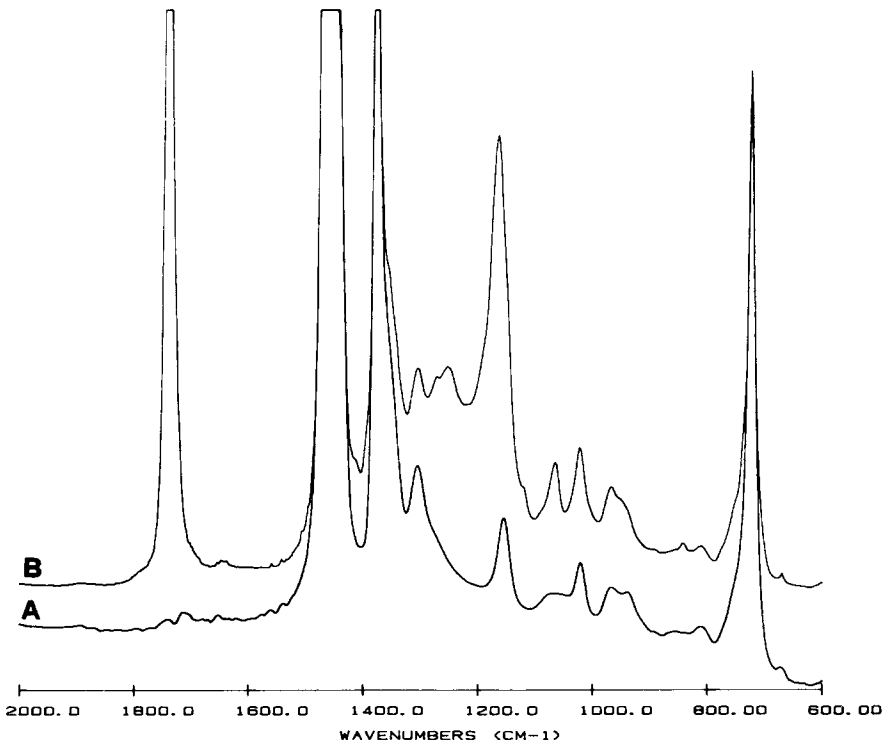
Fig. 4.   Infrared spectra in the region 2000–600 cm^{-1} for (A) EPR-0; (B) EPR-3.7.

film thickness, is presented in Figure 5 for all the investigated copolymers. A linear lowering of the absorbance with increasing the degree of grafting is found, as shown in Figure 6.

The WAXS powder spectra of the EPR and of the functionalized EPRs are shown in Figure 7. The spectra were recorded on compression-molded samples annealed for 15 days at 25°C since, as in the case of the DSC experiments, the intensity of the crystalline peak slowly increases with time reaching the final value after about 15 days.

The WAXS profile of the parent elastomer presents, at about 21.5° of 2θ, a crystalline reflection, identified as the (110) polyethylene strongest reflection;[8–10] its intensity strongly decreases with increasing the grafting degree. For the highest values of degree of grafting ($\geq 10\%$) in the 2θ region 21–23°, only a very weak shoulder superimposed to the amorphous halo can be observed. From the WAXS profiles the crystallinity degree X_c was calculated according to the Hermans-Weidinger method,[11] from the ratio between the crystalline area (A_c) and the total diffracted area ($A_c + A_a$):

$$X_c = 100 \cdot \frac{A_c}{A_c + A_a}$$

The X_c values plotted as a function of the grafting degree (Fig. 8) show a linear decrease with increasing GD. Because of the shape of the WAXS
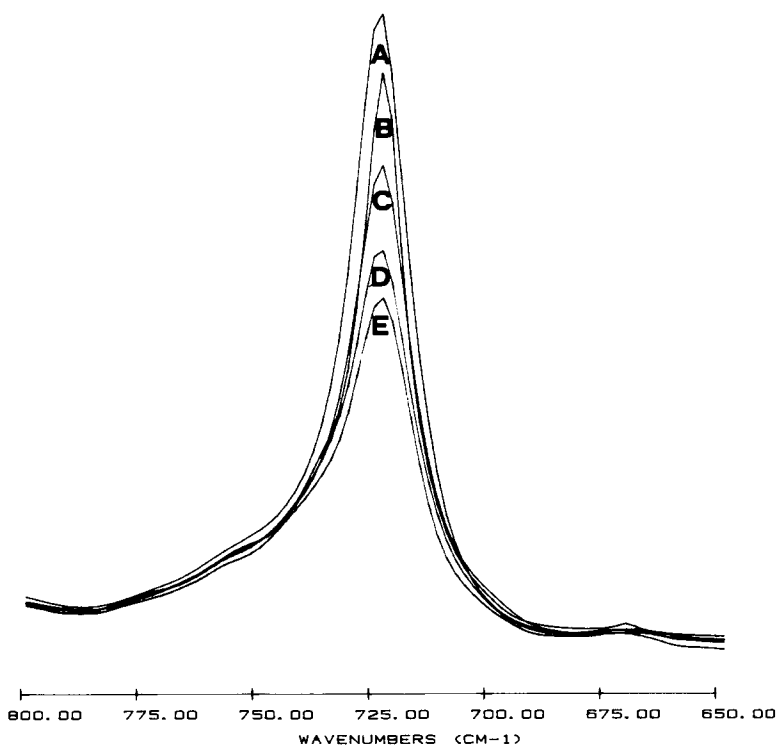
Fig. 5. Infrared spectra in the 900–700 cm^{-1} region for (A) EPR-0; (B) EPR-3.7; (C) EPR-5.1; (D) EPR-10; (E) EPR-13.

profiles, the crystallinity determination becomes more and more uncertain as the GD increases (the estimated error ranges from 5 to 20%). The evaluation of this parameter in elastomers is a difficult task, especially from WAXS patterns obtained by continuous scanning. Work is in progress to determine more accurately the "residual crystallinity" in elastomers having $X_c < 2\%$.
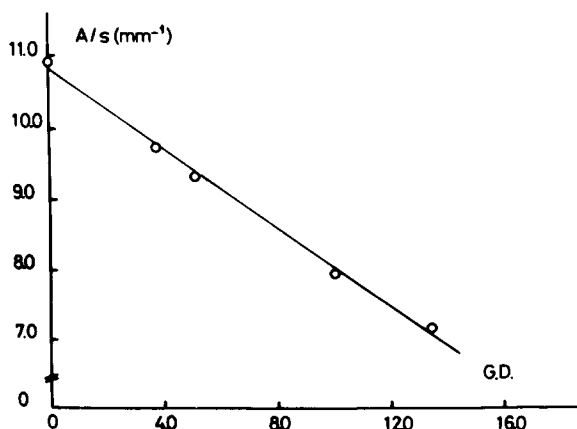

Fig. 6. Dependence of the normalized absorbance, A, of the 721 cm^{-1} band on the grafting degree GD for the investigated elastomers.
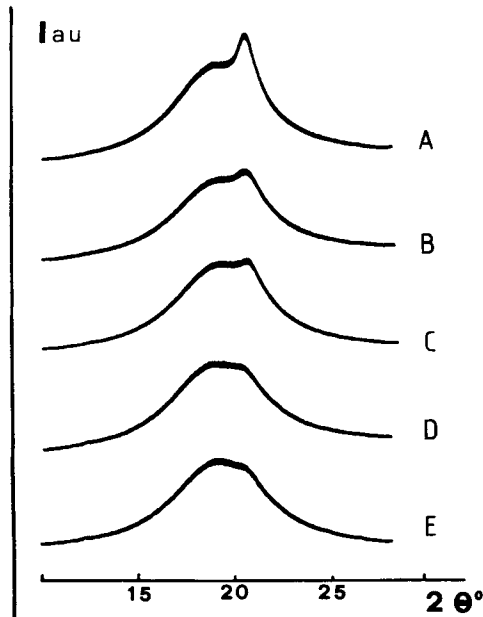
Fig. 7. WAXS powder spectra of the investigated elastomers after 15 days at 25°C: (A) EPR-0; (B) EPR-3.7; (C) EPR-5.1; (D) EPR-10; (E) EPR-13.

A correlation between the X_c values obtained by WAXS and DSC techniques has been attempted: Figure 9 graphically represents the relationships between WAXS and DSC crystallinities, the latter evaluated considering the overall melting enthalpy (curve A) or the enthalpy of fusion relative to peak 2 only (curve B). The curve A deviates from linearity, especially at the highest X_c values, whereas a fine linear relationship is observed for the B case. These behaviors can be ascribed to the fact that the
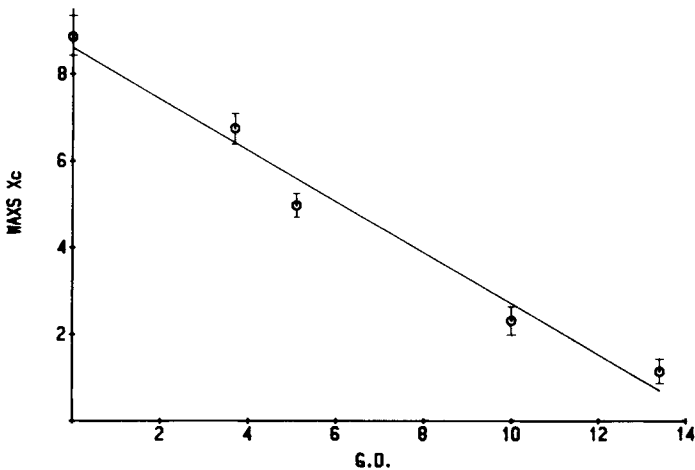

Fig. 8. Influence of the grafting degree GD on the WAXS crystallinity degree of the investigated elastomers.
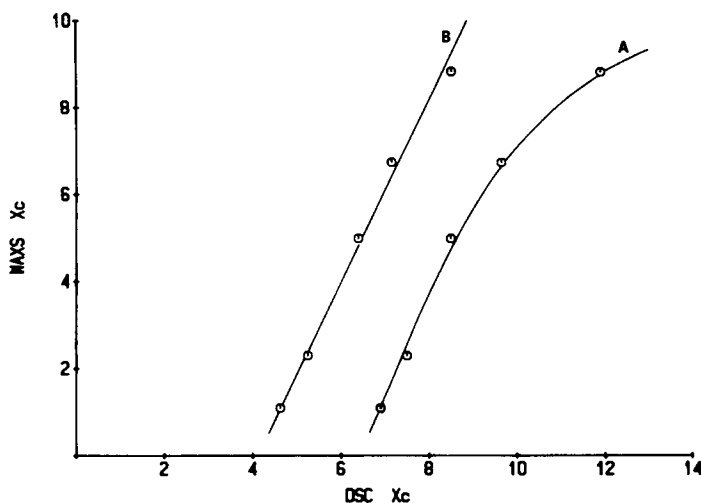
Fig. 9. Relationships between WAXS and DSC crystallinity degrees, the latter evaluated considering the overall melting enthalpy (curve A) or the enthalpy of fusion relative to peak 2 only (curve B).

WAXS spectra are recorded at room temperature and therefore do not reveal the already melted crystalline structures responsible of the melting peak 1 in the DSC thermograms. The DSC crystallinity values are in any case higher than those obtained by WAXS contrary to the few literature data on EPR copolymers:[9] this, in our opinion, is due to the fact that in the WAXS profiles of elastomers having rather low crystallinity, the weak crystalline peak, convoluted with the large amorphous halo, is likely underestimated by the method used.

The results of DSC, IR, and WAXS investigations indicate that the grafting involves to a large extent the methylene sequences by which the crystalline regions of the copolymers are built up and, consequently, the "residual crystallinity" of EPR is strongly reduced by the functionalization process. This finding is in agreement with the conclusions drawn in previous papers[3-5] which showed that in EPRs, because of steric effects, grafting preferentially occurs by addition of the bulky DBM molecule to secondary macroradicals.

With increasing the grafting degree, ΔH_2 significantly decreases while ΔH_1 appears almost unaffected. This suggests that most of the grafting involves secondary macroradicals having the radical sites which belong to long methylene sequences, that is, sites which are far away from C_3 units. This latter effect could be also interpreted assuming that both short and long $-(CH_2)-$ sequences are equally involved in the grafting process. However, after the grafting of a DBM molecule onto the longer methylene sequences, they become shorter and less regular ones, characterized by a lower T_m close or coincident with T_{m1}.

The first hypothesis appears, in our opinion, more convincing. The results obtained on the functionalization of EPRs having the same chemical composition and a different monomer sequence distribution[5] showed, in fact, that a block-like character of the parent elastomer (i.e., an increased tendency to
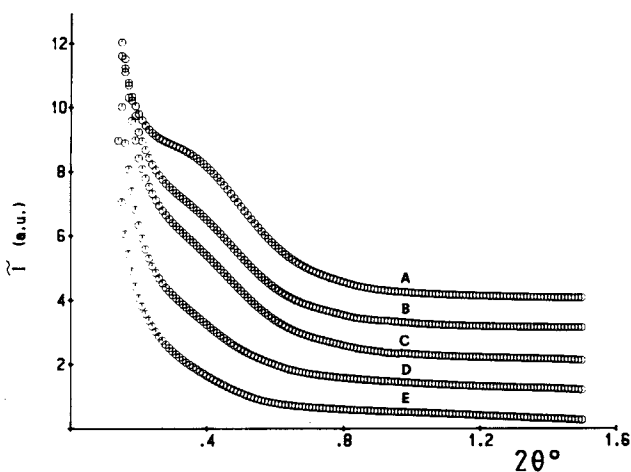
Fig. 10. SAXS profiles of the investigated elastomers: (A) EPR-0; (B) EPR-3.7; (C) EPR-5.1; (D) EPR-10; (E) EPR-13.

form longer and more regular monomer sequences) results in faster kinetics and a higher efficiency of the grafting reaction.

SAXS Superreticular Investigations

The shape of the SAXS profiles of the investigated elastomers (Fig. 10) shows rather weak and rapidly decreasing interferential effect superimposed to a noticeable particle scattering for A, B, and C curves, while the D and E profiles present only a "practically continuous" scattering characteristic of diluted solutions or liquid systems.* For this reason the correction for the slit height was not applied.[12,13]

According to the general theory of Hosemann and Bagchi,[13] the intensities, I, of the above SAXS profiles are plotted (Fig. 11) as $u^2 I$ versus u, where $u = (2 \sin \theta)/\lambda$. By this method the superreticular ("long range") order of the investigated elastomers is strongly evidenced: in the Hosemann's plots, a sharp peak, centered at $1/u \simeq 185$ Å, emerges for the unmodified elastomer and for the B, C, and D profiles. An almost complete absence of interferential effects is observed only for E profile. Both the height and the sharpness of the peak gradually decrease by enhancing the grafting degree.

By the Hosemann treatment, it is possible to obtain a number of parameters from the SAXS data, which give quantitative information about the superreticular ordering levels of the investigated system. From the maximum position, one obtains the so-called "long period," that is, the main distance, between the centroids of adjacent particles. Moreover, from the same plots we can get the values u_m and u_0, where the function ($u^2 I$ versus u) has its maximum and where the tangent at the inflection point intersects the abscissa, respectively. Their ratio $M^* = u_0/u_m$ is indicative of the polydispersity of the "particles" dimensions (°), while the area under the peak, which represents the integrated small-angle scattered intensity, is indicative of the electronic density fluctuation of the system.

*Let us remember that "particle" here must be taken in the broadest sense to include regions of different electronic density.[13]
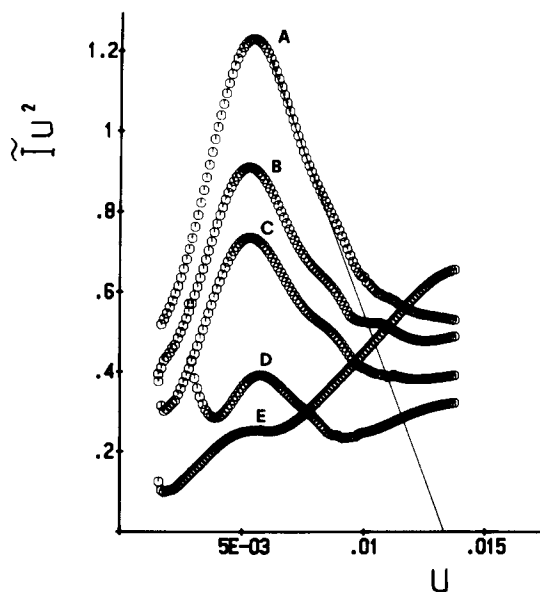
Fig. 11. Hoseman's plots of the SAXS profiles of Fig. 10; $I =$ scattered intensity and
$$\mu = (2\sin\theta)/\lambda.$$

These superreticular parameters are summarized in Table II and in Figure 12. It is observed that the long period does not show appreciable variations, while the M^* values increase exponentially with degree of grafting. Finally a linear dependence is found between the integrated scattered intensity, I or Q, and the grafting degree.

The whole of the SAXS results can be interpreted on the following bases:

1. A significant degree of structuring, at superreticular level, is present in the parent elastomer.
2. The functionalization reaction strongly increases the polydispersity and, at the same time, drastically reduces the electronic density fluctuation in the

TABLE II
SAXS Profiles Analysis Following Hosemann (see Figure 11)

Elastomer	GD (wt%)[a]	u_m (Å^{-1})[b]	u_0 (Å^{-1})[c]	d (Å)[d]	M^*	I (cm^2)	I/I_0 (%)
EPR-0	0	0.00543	0.0115	184	2.12	66	100
EPR-3.7	3.7	0.00532	0.0120	188	2.26	43	65
EPR-5.1	5.1	0.00532	0.0130	188	2.45	37	56
EPR-10	10.0	0.00578	0.0191	173	3.30	7	11
EPR-13	13.4	—	—	—	—	0	0

[a] Degree of grafting.
[b] Abscissa corresponding to the maximum.
[c] Abscissa corresponding to the intersection with the tangent at the inflection point.
[d] Interparticle distance.
Parameters: $M^* = u_0/u_m$, I = integrated scattered intensity, I_0 = integrated scattered intensity of the ungrafted elastomer.
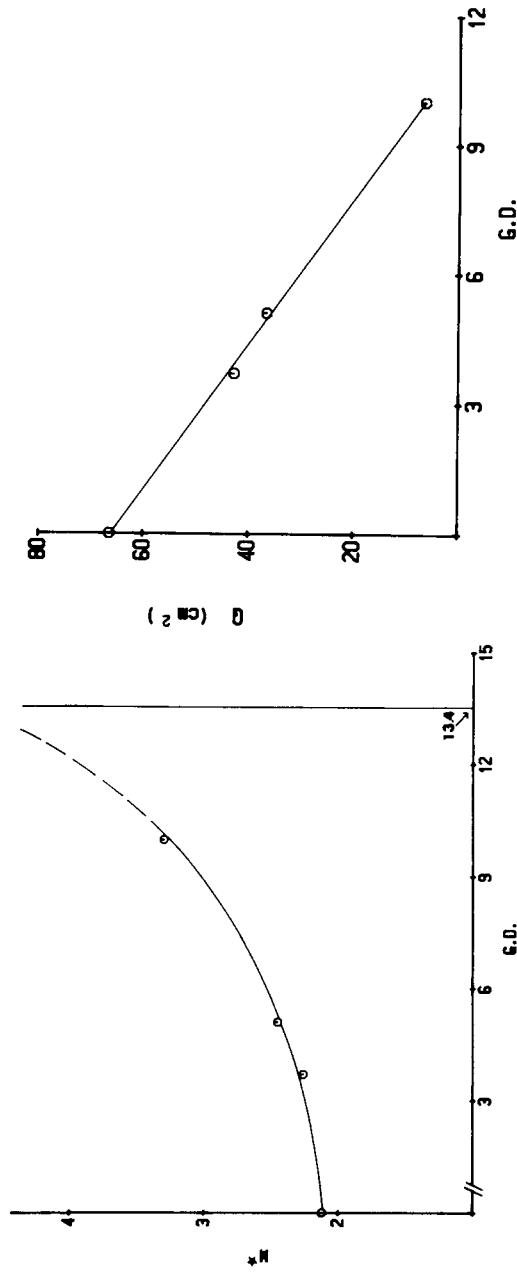
Fig. 12. Influence of the grafting degree, GD, on the M^* parameter (Left) and on the integrated scattered intensity, Q (Right).

system. This could be due to the fact that, by increasing the grafting degree, the number of structured zones decreases and/or these paracrystalline "superreticles" become more and more "distorted," gradually approaching a completely liquid-like system.

A deeper SAXS profiles analysis is currently underway to develop a model based on superreticular parameters such as the "particles" dimensions, their polydispersity and their packing density.[12,13]

CONCLUSIONS

The bulk functionalization of an EPR copolymer ($C_3 = 28\%$ by weight) leads to a linear decrease of the polyethylenic "residual crystallinity" X_c with increasing the grafting degree: The X_c values, evaluated both by WAXS and DSC techniques, drop from 9% for the unmodified elastomer to 1% for the copolymer having the highest grafting degree (13.4%).

The results obtained by various techniques (IR, DSC, WAXS, and SAXS) suggest that the grafting preferentially occurs onto the longer or more perfect methylene sequences of the EPR.

The SAXS profiles, after Hosemann's treatment, evidence a significant degree of structuration, at superreticular level, in the parent elastomer; by increasing the grafting degree the "superreticle" becomes more and more "distorted," gradually approaching a completely liquid-like system.

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