Synthesis and Characterization of EPDM Films

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ABSTRACT: A series of ethylene–propylene-2-ethylidenebicyclo[2.2.1]hept-5-ene terpolymers have been prepared using the $VOCl_3/Al_2Et_3Cl_3$ catalyst under various initial Al/V ratios and diene concentrations. The V/C and Al/V ratios in EPDM films were determined by Rutherford backscattering spectrometry. The concentration of incorporated vanadium increases with the increase of the iodine number, i.e., with the number of double bonds in the polymer. However, the concentration of incorporated V in the terpolymers remains relatively low, which is attributed to the small percentage of V(III) active species due to the presence of the diene. On the other hand, the Al/V molar ratio in the terpolymers was seen to be roughly constant (between 6 and 8), independent of the iodine number and of the initial Al/V molar ratio in the reaction mixture. The polymerization yield was seen to increase with the augmentation of the initial Al/V ratio and of the diene concentration, until reaching a maximum of about 500 g polymer/g V. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 535–541, 1998

Key words: EPDM; aluminum; vanadium; Rutherford backscattering spectrometry

INTRODUCTION

The ethylene–propylene–diene (EPDM) elastomers present excellent physical, mechanical, and chemical properties that guarantee a wide range of applications, as corroborated by their worldwide production higher than 650,000 tons/year.[1] The saturated hydrocarbon nature of the polymer backbone (randomly distributed ethylene and propylene monomer units) is responsible for their excellent resistance to ozone and UV radiation, as well as to acids and alkalis. Besides, the incorporation of a small percentage of ethylenic unsaturations (introduced by a diene termonomer) provides reactive sites, which allow curing by peroxides or sulfur derivatives.[2] Recently, the carboxylation or sulfonation of EPDM has been proposed to produce ionic thermoplastic elastomers.[3,4]

The production of EPDM grades can be modulated by the proper choice of monomer ratio, reaction temperature, catalyst precursor, as well as catalysts, cocatalyts, and diene concentrations. These terpolymers are usually obtained using soluble transition metal compounds (generally V, Ti, or Zr) as catalysts, associated with alkylaluminum as cocatalyst. At the end of the process the metal catalyst and cocatalyst are not completely eliminated from the resultant terpolymers, which may have a deleterious effect. In commercial terpolymers, for instance, the concentration of vanadium must not exceed 10 ppm to avoid coloring, aging, and toxicity.[2] Thus, the determination of metal concentrations incorporated in polymers can lead, in principle, to very useful informations about the polymerization reaction and can allow the establishment of correlations with physicochemical properties of these materials.

The determination of the concentrations of incorporated metallic species in the polymers was reported in recent publications, in the search for different informations. The transport of Ni and Cu against a concentration gradient through a carboxylic membrane was studied by determining their concentration on both sides of the membrane

by complexometry with EDTA.[5] Titrimetric procedures were also employed to estimate metal content present in polymers on which metal complexes were supported.[6] The quantitative determination of Fe(III), grafted onto poly(N-vinylcarbazole) as Fe(III)-phthalocyanine, was attempted by phenantroline spectroscopic method.[7] The phosphorous contents in polyimides, incorporated to improve their solubility and processability, was determined by phosphorous elemental analysis via a microdigestion apparatus with a spectrophotometer.[8] Peak wavenumber derived from polysaccharides FTIR spectra were quantitatively correlated to Na and Ca content.[9] The Zn chelate affinity of polymethacrylate microsphere was estimated by atomic absorption spectrophotometry.[10] The metal extraction ability of sulfur-chlorinated Jojoba wax bound to polystyrene beads was evaluated by inductive coupling plasma (ICP) emission spectroscopy.[11] The same technique was used to determine Ce in low-density polyethylene.[12]

In the present work we report on the metal contents incorporated in EPDM, synthesized using $VOCl_3$ as the catalyst, in the presence of $Al_2Et_3Cl_3$ as the cocatalyst, and with 2-ethylidenebicyclo[2.2.1]hept-5-ene (ENB) as the diene. V/C and Al/V ratios were determined by Rutherford backscattering spectrometry (RBS), and correlated with the polymerization yield. The metal content incorporated in polymers was also studied by varying the initial Al/V molar ratio and the initial diene concentration.

EXPERIMENTAL

Chemicals

Polymerization grade ethylene and propylene were purchased from White-Martins and dried using molecular sieve (0.4 nm) columns. Hexane was dried by refluxing over metallic sodium followed by distillation under argon atmosphere. 2-Ethylidenebicyclo[2.2.1]hept-5-ene (ENB), the catalyst precursor $VOCl_3$ (0.23M in hexane), and the cocatalyst $Al_2Et_3Cl_3$ (1.00M in hexane) were donated by Nitriflex S.A.

Polymerization Reactions

The polymerizations were carried out in a 2-L glass reactor (Büchi) using hexane as the solvent. The diene, the vanadium compound, and the re-

quired amount of cocatalyst were introduced in this order into the reactor containing hexane (1 L) under positive pressure of a mixture of ethylene and propylene (1 : 3 in mass, according to gas chromatography analysis of the gas phase) at 273 K. The temperature was then increased to 288 K and maintained at this temperature, under continuous flow of ethylene and propylene, for 30 min. The reaction was then quenched by the addition of ethanol at room temperature. The polymer was collected, washed with ethanol (1 L), and vacuum dried at 423 K for 60 min. Circular polymer films (70 mm wide and 0.15 mm thick) were produced by pressing the dried polymers under 12 MPa at 423 K.

Polymers Characterization

The polymer films were characterized by infrared spectroscopy (Mattson 3020 FTIR spectrophotometer) measuring the ratio of the intensities of the 1155 cm^{-1} methyl band and the 720 cm^{-1} methylene band according to the ASTM D3900. The diene incorporation was monitored by the intensity of the 817 cm^{-1} band and compared to those obtained from commercial polymer samples with known iodine numbers.

The glass transition temperature (T_g) of the polymers was determined using differential scanning calorimetry (12000 PL-DSC) with a heating rate of 20 K min^{-1}, while the viscosity molecular weight (M_v) was determined with an Ubbelohde type viscometer using decalin as solvent at 408 K.

Rutherford Backscattering Spectrometry (RBS)

Ion beams have been used recently to characterize and to determine diffusion coefficients in polymers.[13–18] In the present work, RBS was used to determine the atomic ratios V/C and V/Al in EPDM polymer films. Because RBS is not very well known by chemists, an introductory overview of the principles and capabilities of this technique is presented in the following. The principle of RBS is to place a sample in the pathway of a monoenergetic ion beam coming from an ion accelerator, and to detect the particles that are elastically scattered in the coulombic field of the sample atomic nuclei. The most common incident beam is $^4He^+$ and the detector (normally a surface barrier detector is used to detect the scattered particles) is usually placed at 165° with respect to the incidence
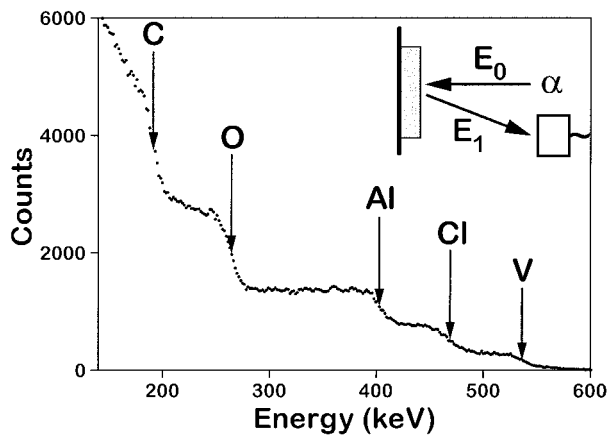
Figure 1 Typical Rutherford backscattering spectrum of an EPDM thin film. The arrows indicate the outermost (surface) position of the corresponding elements in the sample. A scheme of this geometry, also showing the sample and the detector, is sketched in the top of the figure.

direction of the beam, characterizing a backscattering geometry (see the scheme sketched in the top of Fig. 1). The energy of the scattered particles depends among other factors,[13] on the incidence energy, on the atomic mass of the atoms involved in each specific backscattering event, and on the depth in the sample where the scattering event occurred.

In Figure 1 is shown a typical RBS spectrum. The channel number (X-axis) has a linear dependence on the energy of the scattered particles. So, the spectrum is the backscattering yield (number of detected particles backscattered with a certain energy) as a function of the energy of these backscattered particles. For a given atomic mass and energy of the incident particles, it can be seen in Figure 1 (M_{inc} = 4 a.m.u., E_{inc} = 0.8 MeV) the effect of the various masses of the atoms constituting the target: the greater the atomic target mass, the greater will be the energy (or the channel number) of the detected scattered particles due to the smaller energy and momentum transfer to the recoiling target nuclei. In the case of the present work, the samples were polymer films produced by pressing the dried polymers (see Polymerization Reactions section). When an incident particle penetrates the polymer film, it looses kinetic energy by interactions with the electrons of the medium before and after being scattered by the nuclei. The kinetic energy that is lost depends on the composition of the sample and on the length of the trajectory (or depth) of the incident

ion in the material. Thus, an incident particle that is scattered by an atom at the sample surface will come out with an energy greater than another one scattered by the same kind of atom at a certain depth in the bulk of the sample. As the energy lost by interactions with electrons is continuous in a macroscopic scale, it is observed experimentally a continuous signal starting at the energy edge (see the arrows in Fig. 1 corresponding to a scattering by an atom of a certain species at the surface) and continuing towards lower energies. The fact that the leading edges in the signals corresponding to each species in the polymer film are not abrupt is mainly due to the rugosity of the film surfaces. The RBS spectrum shown in Figure 1 consists of V, Cl, Al, O, and C signals, each one giving more or less rectangular contributions, which summed up constitute the experimental spectrum. The height of the signal is proportional to the probability of such a scattering event to occur, which depends on the density (in fact, the surface density) of that atomic species in the polymer sample and on the scattering cross section. The scattering cross section is proportional, among other factors, to $(Z_1 Z_2 / E)^2$ where Z_1 and Z_2 stand for the atomic numbers of the incident and target particles, respectively, and E is the energy of the incident particle immediately before the scattering. So, for a given incident particle ($^4He^{++}$ in our case), if the densities of C and V atoms in the sample were the same, the V signal would be 14.7 times more intense than the C signal, according to the ratio Z_V^2 / Z_C^2. This property renders RBS very sensitive to detect small traces of heavy elements in a lighter matrix. The $(1/E)^2$ dependence of the scattering cross section is responsible for the "tail" towards higher number of counts observed at low energies. At high energies this trend is not so evident, and a homogeneous depth profile will correspond to a flat signal, as in the signals of Al, Cl, and V, evidencing, in the present case, the samples depth homogeneity. Because the height of the signal is proportional to the density of that element in the sample, the atomic ratios can be calculated by converting the signal height ratios (V/Al or V/C) into atomic ratios,[13] and then the molar ratios can be obtained. In fact, the calculations of the present work, based on the heights of the signals in the RBS spectra, were made using the full expression for the differential Rutherford scattering cross section[13] that considers not only Z_1, Z_2 and E, but also the detection angle and the atomic masses.

The experimental setup to perform RBS consists of an ion accelerator on line with an analysis chamber, in which the base pressure must be smaller than 10^{-6} mbar, and the electronics concerned to counting and classifying the detected particles according to their energy (preamplifier, amplifier, multichannel analyzer, etc.). The RBS spectra of the present work were obtained using the 500 kV HVEE Ion Implanter of the Instituto de Física, UFRGS, in Porto Alegre. The incident $^4He^{++}$ beam had an energy of 0.8 MeV. The incidence angle was 0° with the sample normal, and the detection angle was 165° with respect to the incidence direction of the beam. The errors involved in the detection, counting, and calculation of the stoichiometric ratios lead to an overall error of 10% in the atomic ratios.

RESULTS AND DISCUSSION

Synthesis and Characterization of EDPM

The ethylene–propylene-2-ethylidenebicyclo[2.2.1]hept-5-ene terpolymers have been prepared using the classical $VOCl_3/Al_2Et_3Cl_3$ catalytic system under various initial Al/V ratios and diene concentrations. The Al/V ratios in the present work are expressed in terms of the number of mol of Al divided by the number of mol of V. As the cocatalyst has two Al atoms per molecule, and in polymer publications it is usual to express this concentration as the number of Al containing molecules divided by the number of moles of V, a simple way to convert our initial solution data into the above-mentioned ratio is to multiply them by 2.

The characterization of the polymers here obtained by viscometry and IR lead to the results summarized in Table I, which coincide with the characteristics usually observed[2] for the products of this type of polymerization reaction.

Effect of the Initial Al/V Ratio

Figure 2(a) shows that the polymerization yield increases with the initial Al/V molar ratio in the solution (for a constant initial diene concentration of 1.8×10^{-3} mol/L) up to 500 g EPDM/g V, when the curve reaches the saturation, in agreement with previous reports.[2]

The Al/V molar ratio incorporated in the polymers as a function of the initial Al/V molar ratio in the solutions (for a constant initial diene con-

Table I   Reaction Parameters and Physicochemical Characteristics of the Terpolymerization Reaction Products

Initial Al/V (mol/mol)	Initial [diene] (10^{-3} mol/L)	M_v (10^6 a.m.u.)	Ethylene in Polymer (%)
1.3	1.8	1.7	53
2.5	1.8	—	45
4.2	1.8	1.1	41
5.0	1.8	—	41
7.5	1.8	0.7	39
4.2	1.0	0.9	40
4.2	5.0	0.8	44
4.2	9.0	0.2	45
4.2	18.0	—	49

Some entries for the viscosity molecular weight (M_v) could not be obtained due to crosslinking that prevented the polymers solubilization.

centration of 1.8×10^{-3} mol/L) are given in Figure 2(b). One notices that the Al/V molar ratio incorporated in the polymers remains roughly constant (between 6.0 and 7.5) for all the analyzed range of initial Al/V ratios in the solution. Moreover, the incorporated Al/V molar ratios are higher than the initial ones, which lead us to believe that the V contents in the final polymers are lower than those present in the initial solution. It was already shown that the diene deactivates V(III) species into V(II).[19] Thus, such inactive species would be washed out, letting only V(III) species to be responsible for the catalytic activity. If we consider, in accordance with ref. 19, that only 18% of the V in the reaction milieu is present as active species, the corresponding incorporated Al/V ratio would be between 6 and 7.

According to Table I, as the initial Al/V molar ratio increases (for a constant initial diene concentration of 1.8×10^{-3} mol/L), the viscosity molecular weight decreases sharply, probably due to the chain transfer termination caused by the alkylaluminum, which is in excess. On the other hand, the ethylene incorporation in the polymer is seen to be high for low initial Al/V molar ratios. One can attribute this fact to the higher ethylene reactivity, compared to propylene, which guarantees its insertion in the rare active species, present in such low Al/V ratio. These two facts were recently observed in dynamic simulation.[20]

One advantage of these polymer systems is that all measured T_g remained constant around 232 $\pm$ 1 K, in this range of incorporated ethylene and
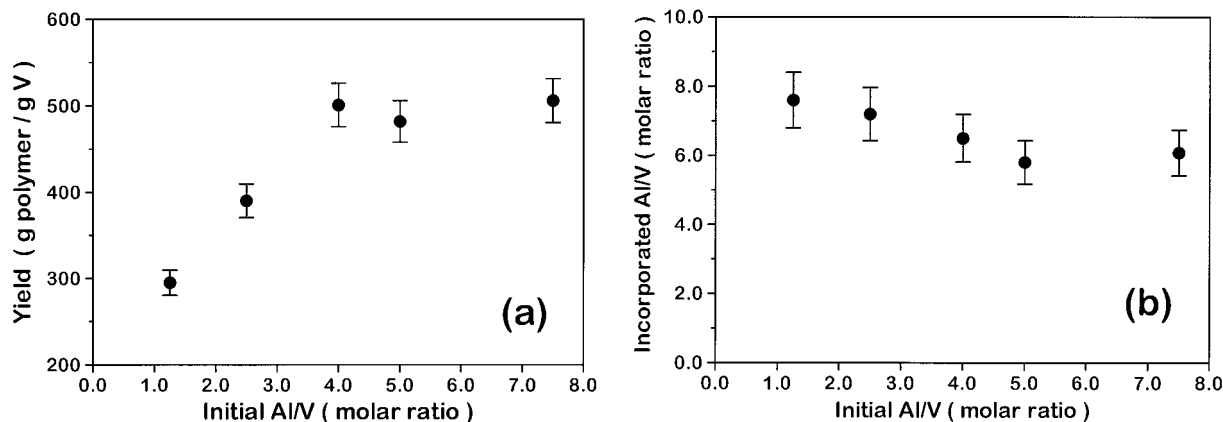
Figure 2 (a) Dependence of the polymerization yield, and (b) dependence of the Al/
V ratio incorporated in the polymer on the initial Al/V ratio in the reaction mixture
keeping the initial diene concentration constant at 1.8×10^{-3} mol/L.

diene. Thus, the same processing conditions of the resultant polymers can be set for a number of grades.

Effect of Diene Concentration

Figure 3 shows that the polymerization yield remains constant (around 500 g EPDM/g V) when the ENB concentration varies in the range 5 to 18×10^{-3} mol/L, if the Al/V molar ratio in the solution is kept constant at 4.2 [value that corresponds to the beginning of the saturating behavior in Fig. 2(a)].

Figure 4 shows the Al/V and the V/C molar ratios incorporated in the polymers (for a constant initial Al/V molar ratio in the solution of 4.2) as
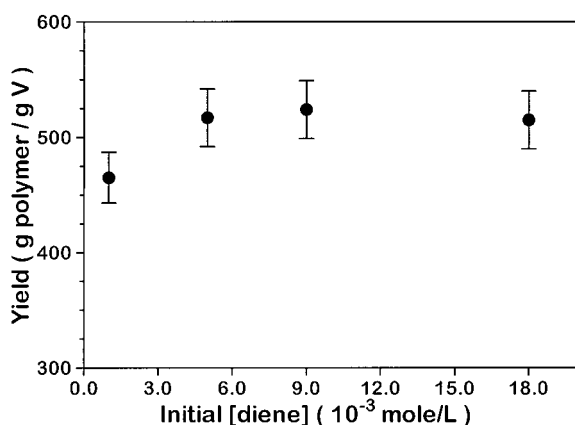

Figure 3 Dependence of the polymerization yield on the initial diene concentration in the reaction mixture keeping the initial Al/V molar ratio constant at 4.2.

a function of the iodine number (i.e., the number of double bonds) in the polymer. According to Figure 4(a), the incorporated Al/V molar ratio remains constant in all range of analyzed iodine numbers of the polymer. On the other hand, the V/C ratio (essentially the V concentration in the polymer) is roughly constant (around 150 ppm) up to iodine number 25, and then increases for higher iodine numbers [Fig. 4(b)]. Because Al/V is constant according to Figure 4(a), the Al amount should increase proportionally to the increase of V, for iodine numbers greater than 25. In such catalyst systems, the proposed active species possesses alkylaluminum molecules coordinated to the vanadium complex.[21] The present results seem to follow this trend, because the Al/V ratio remains constant in the polymer. Moreover, the observation that the V content increases with the diene concentration indicates that the V atoms must interact somehow with unsaturations present in these polymers, besides their participation on the polymeric chain.

According to Table I, it is also noticeable that M_v decreases with the increase of the initial diene concentration (for a constant initial Al/V molar ratio of 4.2). This fact can also be explained taking into account that the diene can inactivate the V catalytic species by reduction of the V(III) active species to the V(II) inactive one,[19] leaving more Al available in the milieu to act at the chain transfer step, and consequently leading to smaller polymer chains. On the other hand, the ethylene concentration incorporated in the polymer increases with the initial diene concentration (for a con-
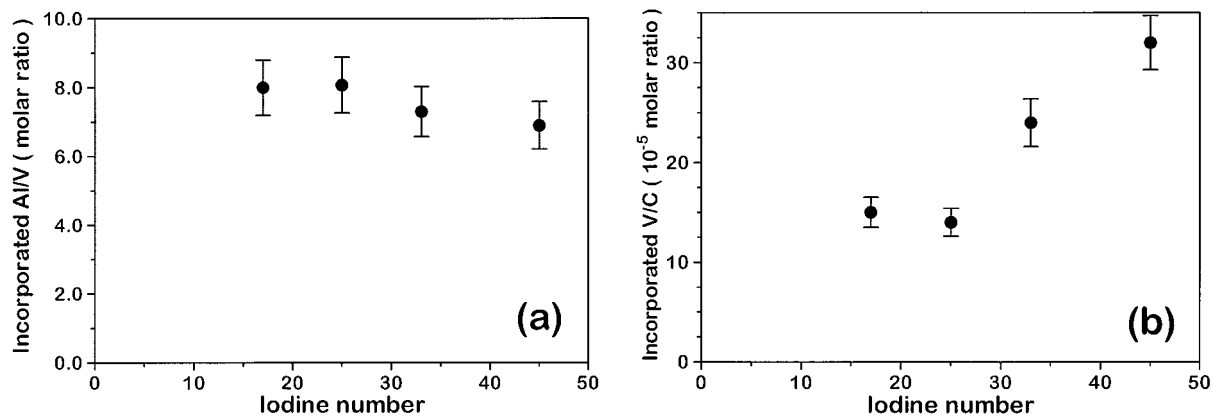
Figure 4 Dependence of the incorporated (a) Al/V and (b) V/C ratios on the number of double bonds in the polymer (expressed by the iodine number) for an initial Al/V molar ratio of 4.2 in the reaction mixture.

stant initial Al/V molar ratio of 4.2) probably because the reactivity of a diene terminated polymer chain is higher with ethylene than with propylene.[2]

CONCLUSIONS

In summary, in the present work an initial Al/V molar ratio around 4.0 led to the optimal polymerization yield, confirming previous data. The incorporated Al/V molar ratio in EPDM was seen to be independent of the Al/V molar ratio used in the polymerization reaction, and also independent of the concentration of double bonds in the polymer. The Al/V incorporated ratios are higher than those initially present in the solution, probably due to the low concentration ($\sim$ 18%) of V (III) active species caused by the presence of the diene. Nevertheless, taking into account that the concentration of incorporated V increases, and the incorporated Al/V ratio is constant for increasing amounts of incorporated diene in these terpolymers, the Al content on the EPDM thin films must also increase, leading one to propose that Al remains coordinated to V in the terpolymer. The behavior of the polymer properties under our experimental conditions is attributed to chain transfer termination (high Al/V ratio), higher ethylene reactivity (evident for low Al/V ratio) and diene termination (for high diene concentration). The RBS technique was seen to be adequate for the determination of the Al/V and V/C ratios, especially due to the intrinsically simple sample preparation and quickness of the analysis ($\sim$ 15 min/

spectrum). Further work on the characterization of the terpolymers is in progress, especially concerning the determination of metal depth profiles and segregation.

REFERENCES

1. International Institute of Synthetic Rubber Producers, Inc., Houston, TX, 1995.
2. G. V. Strate, in *Encyclopedia of Polymer Science and Engineering,* H. F. Mark, N. M. Bikales, C. G. Overberger, and J. J. Koschwitz, Eds., J. Wiley & Sons, New York, 1973, p. 522.
3. S. Datta, S. K. De, E. G. Kontos, J. M. Wefer, P. Wagner, and A. Vidal, *Polymer,* **37,** 3431 (1996).
4. T. Kurian, D. Khastigir, P. P. De, D. K. Tripathy, S. K. De, and D. G. Pfeiffer, *Polymer,* **37,** 4865 (1996).
5. I. Alexandra, and G. Iordanov, *J. Appl. Polym. Sci.,* **63,** 9 (1997).
6. T. Kaliyappan, C. S. Swaminathan, and P. Kannan, *Eur. Polym. J.,* **33,** 59 (1997).
7. T. Zamora, and M. C. Gonzalez, *Polymer,* **38,** 263 (1997).
8. Y.-L. Liu, G.-H. Hsiue, C.-W. Lan, J.-K. Kuo, R.-J. Jeng, and Y.-S. Chiu, *J. Appl. Polym. Sci.,* **63,** 875 (1997).
9. C. Sartori, D. S. Finch, B. Ralph, and K. Gilding, *Polymer,* **38,** 43 (1997).
10. A. Denizli, G. Köktürk, B. Salih, A. Kozluca, and E. Piskin, *J. Appl. Polym. Sci.,* **63,** 27 (1997).
11. S. Binmam, S. Belfer, and A. Shani, *J. Appl. Polym. Sci.,* **63,** 625 (1997).
12. Y Lin, *J. Appl. Polym. Sci.,* **63,** 811 (1997).
13. P. F. Green and B. L. Doyle, in *New Characteriza-*

tion Techniques for Thin Polymers Films, H.-M. Tong and L. T. Nguyen, Eds., J. Wiley & Sons, New York, 1990, p. VI/139 ff.

14. L. J. Matienzo, F. Emmi, D. C. Van Hart, and T. P. Gall, *J. Vac. Sci. Technol.,* **A7,** 1784 (1989).
15. R. M. Papaléo, M. A. de Araújo, and R. P. Livi, *Nucl. Instrum. Methods,* **B65,** 442 (1992).
16. R. B. Guimarães, L. Amaral, R. P. Livi, J. P. de Souza, M. Behar, and F. C. Zawislak, *Nucl. Instrum. Methods,* **B 32,** 419 (1988).

17. J. F. Romanelli, J. W. Mayer, E. J. Kramer, and T. P. Russel, *J. Polym. Sci.,* **24,** 263 (1986).
18. P. J. Mills, C. J. Palmstrøm, and E. J. Kramer, *J. Mater. Sci.,* **21,** 1479 (1986).
19. M. Dolatkhani, H. Cramail, and A. Deffieux, *Macromol. Chem. Phys.,* **197,** 289 (1996).
20. M. C. Haag, master's thesis, Instituto de Química, Universidade Federal do Rio Grande do Sul, 1997.
21. J. Chatt and A. Duncanson, *J. Chem. Soc.,* 2939 (1953).