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Synthesis and properties of some EPDM graft terpolymers

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Summary

Two EPDM graft terpolymers, one with polystyrene branches and one with poly-α-methylstyrene, were prepared from a commercial EPDM polymer using "grafting from" techniques. The new materials were characterized by GPC, osmometry and nmr spectrometry; tensile strength properties were also determined.

Introduction

In three previous papers, we reported the syntheses of EPDM graft polymers with branching polyisobutylene (1), polystyrene (2), and poly-α-methylstyrene (3), all prepared from copolymerization of ethylene and propylene with macromonomers of the above polymers carrying the dicyclopentadiene head group.

Another approach to preparing graft polymers is by cationic techniques using appropriate functional groups on the polymer from which cationic polymerization can be initiated. This "grafting from" technique has been exploited by Kennedy and co-workers. For example, Kennedy and Smith have grafted polystyrene from chlorinated EPM polymers, (4) and Kennedy and Vidal prepared bigraft copolymers from a chlorobrominated EPDM terpolymer containing 1,4-hexadiene as the termonomer (5). The same research group also prepared polystyrene grafts of EPM and EPDM by cationic reactions in the melt (6).

In this paper, we report the synthesis and studies on two EPDM graft polymers, which were prepared by cationic polymerization from a commercial EPDM containing 5-ethylidine-2-norbornene (ENB) as the diene.

Experimental

Solvents and Starting Materials. Heptane, methylene chloride, tetrahydrofuran, styrene and α-methylstyrene were purified as described in our earlier papers (2,3). Methyl chloride (Linde) was dried by passing the gas through a column packed with barium oxide and molecular sieves before being condensed for use. t-Butyl hypochlorite was prepared by the procedure of Mintz and Walling (7).

Physical Methods. Infrared and ^{1}H nmr spectrometry, as well as molecular weight measurements, were carried out as described earlier (2,3). The stress-strain behavior of polymer specimens was studied on an Instron Model 4310 tester at a crosshead speed of 5 cm/min. The graft copolymer samples were compression molded on a Dake Press (hydraulic) by using a pressure of 29.86 mega pascal (MPa) at temperatures between 100-150°C.

Chlorination of the EPDM Polymer. In a dry, 1L, single-necked flask was placed 10g of purified EPDM polymer (7.7% ENB by weight and $\overline{Mn}$ = 50,000) and a magnetic stirring bar. The polymer was dissolved in 500 mL of dry heptane, then 20.35 g of t-butyl hypochlorite was added and the reaction mixture was stirred for 2 h while it was irradiated in a Rayonet Photochemical Reactor at 350 nm. The chlorinated polymer was precipitated in acetone, collected by filtration, and purified by redissolving and reprecipitating several times. The final polymer was dried under vacuum at 50°C.

Synthesis of Graft Copolymers by Cationic Grafting Reactions. EPDM-g-PS and EPDM-g-PαMSt graft copolymers were prepared by the following method, starting from chlorinated, commercial EPDM polymer.

Into a 1L, 3-necked flask with a magnetic stir bar, 1.0 g of the chlorinated EPDM and 160 mL of dry heptane were placed. After the polymer was completely dissolved, 50 mL of the dry monomer (styrene or α-methylstyrene) and the desired amount of cosolvent (methyl chloride for styrene and methylene chloride for α-methylstyrene) were added. When methyl chloride was used as the cosolvent, the flask was cooled to -40°C inside a dry box and the methyl chloride was condensed into the flask. Serum caps were placed on three necks, and the flask was quickly taken out of the dry box and placed in a dry ice/acetone bath maintained at -30°C. The reaction mixture was stirred to insure homogeneity, and 10 mL of a precooled 0.35M solution of diethylaluminum chloride in heptane/cosolvent mixture was injected into the flask. Grafting was initiated immediately as evidenced by the turbidity of the solution. Time periods up to 1 min were used for the reactions to achieve the desired conversion of the monomer. The reaction was terminated by introducing 10 mL of precooled methanol into the flask, and the product was immediately precipitated by adding the reaction solvent to a 10-fold excess of acetone. The crude polymer was collected by filtration and the pure graft copolymer was isolated by selective solvent extraction.

Isolation of Pure Graft Copolymers. The isolation of pure EPDM-g-PS was accomplished by dissolving the crude polymer in toluene and precipitating from a 10-fold excess of acetone. Usually, two or three acetone precipitations were required to dissolve all the homopolystyrene. The resulting solid material was extracted with α-heptane to dissolve ungrafted chlorinated EPDM. Two overnight extractions were sufficient for this purpose. The insoluble polystyrene graft copolymer was dissolved in toluene, the solution was filtered, and the material precipitated from methanol. The final graft copolymer was dried under vacuum at 50°C for further characterization.

For the purification of EPDM-g-P-MSt, the above procedure was employed, except 2-pentanone was used instead of acetone.

Results and Discussion

For the chlorination of the commercial EPDM polymer, irradiation in the presence of t-BuOCl was deemed preferable to the use of N-chlorosuccinimide because of its high selectivity for halogen substitution at the allylic position (8, 9). The polymer chosen for chlorination contains 7.7% ENB by weight, and has a molecular weight ($\overline{Mn}$) of 50,000. Therefore, there is an average of 32 ENB units along the polymer chain. When one allylic position per ENB molecule is achieved, the chlorine content will be 2.75%. This was achieved with 2.1 g of t-BuOCl (30.2:1, t-BuOCl:ENB) per gram of EPDM polymer in the chlorination reaction. It is possible to achieve greater amounts of chlorine in the polymer, but this is accompanied by large amounts of gel formation.

Investigation of the chlorinated polymer revealed a molecular weight ($\overline{Mn}$) of 50,000, and molecular weight broadening was not observed in the gpc curve. These results indicate that degradation of the polymer does not occur during the chlorination process.

The "grafting from" technique was employed for the preparation of the graft copolymers. Cationic polymerization of styrenic monomers was initiated from the chlorinated positions using Et_2AlCl.

The solubility characteristic of the EPDM polymer imposed a severe temperature limitation on the experimental conditions. Efficient grafting could only be obtained in the presence of 10-20% of a polar solvent, e.g., methyl chloride or methylene chloride. Since the EPDM polymer is insoluble in polar solvents, a heptane/polar solvent mixture was used as the grafting medium; however, the EPDM polymer did not dissolve in this solvent medium below -30°C. Hence, all grafting reactions had to be carried out at -30°C or above. These relatively high grafting temperatures led to a considerable amount of homopolymer formation, mainly because of chain transfer to the monomer, which decreases the grafting efficiency (GE).

Various amounts of polar solvent (methyl chloride) were used and the effect on the grafting efficiency was studied. The results are shown in Table I. When methylene chloride was used as a cosolvent, the grafting reaction rates were high, and high (>80%) monomer conversions were obtained in a very short time period leading to gel formation. After carrying out a number of preliminary experiments, it was observed that gel formation could be avoided by maintaining the monomer conversion below 25%. When α-methylstyrene was used as the monomer, the grafting reactions were much faster than styrene as the monomer and the α-MeSt conversion was almost uncontrollable. To monitor the α-methylstyrene conversion in these reactions, the coinitiator solution was added dropwise over a very short period of time (0.5 min).

TABLE I
The Effect of Solvent Polarity on GE

Exp	MeCl % vol	St. Conv. %	$\overline{Mn}$ PS	$\overline{Mn}$ Graft	GE %
1	0	2.0	--	--	--
2	5	10.5	8,000	60,000	7.5
3	10	13.2	10,200	59,800	12.0
4	15	19.0	17,100	66,500	18.1
5	20	18.1	15,000	78,500	22.7

Conditions: 0.3 g of Cl-EPDM (2.75% Cl); [Et_2AlCl] = $1.35x10^{-2}$M; [styrene] = 1.5M; solvent = heptane/MeCl; total volume = 85 mL; temperature = -30°C.

The main objective of this research was to synthesize graft copolymers with higher branch/backbone (b/B) ratios. It was thought that by increasing the chlorine content of the EPDM backbone, a higher number of branches could be incorporated into the graft polymers. The effect of changing the chlorine content from 2.0 to 4.0% in the Cl-EPDM backbone on the b/B ratio has been studied and the results are shown in Table II.

TABLE II
Effect of Chlorine Content of Cl-EPDM on the b/B Ratio of the Graft Copolymer

Exp	% Cl in Cl-EPDM	Monomer Conv. %	$\overline{Mn}$(h)*	$\overline{Mn}$ (graft) Obs. Cal.	Glassy Polymer Content % by wt	b/B
1	2.0	10.8	9,500	57,500/59,500	13	0.8
2	2.75	14.0	10,000	68,600/70,000	27	1.86
3	4.0	22.1	15,500	125,000/127,500	60	4.84
4	4.0	20.2	17,000**	99,400/101,000	50	2.91

Conditions: Solvent = heptane/methyl chloride (80/20); monomer conc. = 1.5M; temp. = -30°C; weight of Cl-EPDM = 1.0 g; total volume = 260 mL; [Et_2AlCl] = $1.35x10^{-2}$M]. When α-MeSt was used as a monomer total volume = 265 mL; [M] = 1.45M.

*h = homopolymer

**Homopoly-α-methystyrene

Only a limited number of experiments were possible since our efforts to prepare Cl-EPDM samples containing more than 4.0% chlorine were unsuccessful. In all these experiments, the reaction conditions were essentially the same; only the amount of chlorine in the backbone was varied. All the experiments were terminated at an appropriate time interval to give monomer conversions in 10-25% range.

The main conclusion which can be drawn is that in the limited range of chlorine content studied, the number of chlorine atoms per backbone does have some influence on the branch/backbone ratio. The monomer conversion is higher and a greater number of branches were incorporated into the graft copolymers indicating that a greater number of chlorine sites were activated at higher chlorine content.

The influence of the polarity of the medium on the GE was examined at -30°C by adding various amounts of methyl chloride to the heptane solution of Cl-EPDM. The amount of methyl chloride was varied in the range of 0-20% by volume. The styrene concentration and the total volume of the system were kept constant by decreasing the heptane concentration to compensate for the increased amounts of methyl chloride. The results are shown in Table I. A significant increase in GE was observed with increasing methyl chloride concentration. These observations are in agreement with the results of Kennedy and Smith (4).

In pure heptane medium, a negligible amount of homopolystyrene was formed and no graft copolymer could be isolated. This increase in GE with increasing polar solvent concentration is likely related to the increase in the degree of polymerization with increased dielectric constant of the medium in cationic polymerization.

The efficiency of the grafting process is proportional to the amount of graft polymer (PS or P-α-MeSt), relative to the total amount of polymer formed during grafting and is defined as:

$$\begin{array}{l}\text{Grafting \%}\\ \text{Efficiency}\end{array} = \frac{\text{Grafted Polymer}}{\text{Grafted Polymer + Homopolymer}} \times 100$$

The amount of grafted polymer can be calculated from the weight of the graft copolymer formed and its composition. The exact weight of the homopolymer formed in the reaction can be found by extracting the homopolymer in a suitable solvent and then evaporating the solvent on a rotary evaporator.

The branch/backbone ratio was calculated by the following equation:

$$b/B = \frac{\overline{Mn}\ (g) - \overline{Mn}\ (B)}{\overline{Mn}\ (h)}$$

where $\overline{Mn}$ (g), $\overline{Mn}$ (B) and $\overline{Mn}$ (h) are the number average molecular weights of the graft, the backbone, and the homopolymer isolated from the crude product, respectively.

The validity of the above relation is based on the assumption that the $\overline{Mn}$ of the homopolymer formed is the same as that of the grafted branches. Although there is no conclusive evidence for this assumption, excellent agreement between the predicted (on the basis of $\overline{Mn}$ of the homopolymer) and the observed molecular weights of the graft copolymers supports the assumption. Figure 1 shows the relation between the glassy polymer content of the graft copolymer versus the number average molecular weight of the graft polymer. The solid line demonstates the relationship based on the calculated $\overline{Mn}$ of the graft copolymer.

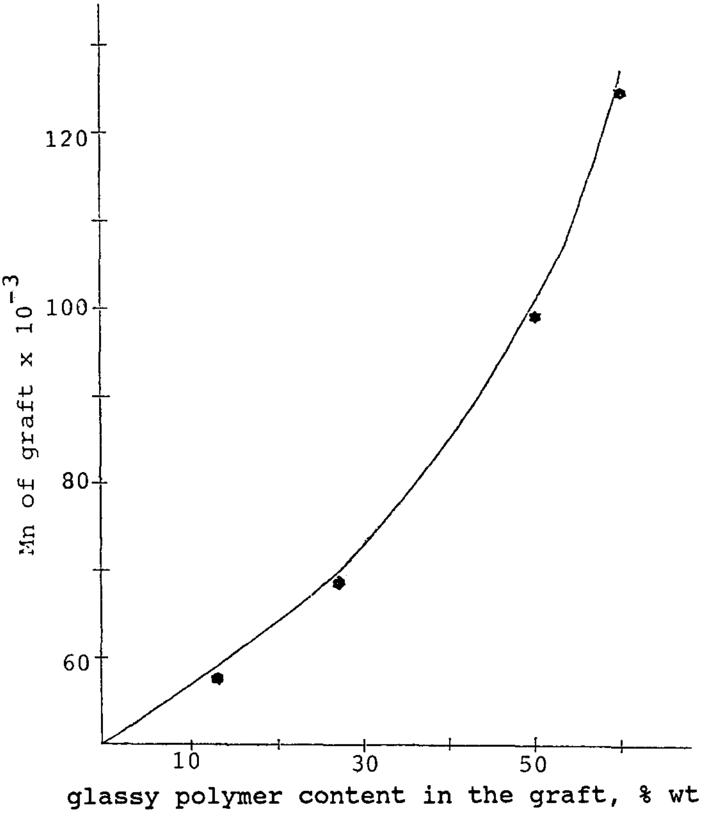

Figure 1
Glassy Polymer Content in the Graft Polymer
versus $\overline{Mn}$ of the Graft Polymer

The graft polymers consist of a rubbery EPDM backbone carrying glassy polystyrene or poly(α-methylstyrene) branches, and can be categorized as thermoplastic elastomers. Films of some graft copolymers were cast from solution, as well as by compression molding. Tensile properties of these films are shown in Table III.

TABLE III
Tensile Properties of the Graft Copolymers

Type of Glassy Polymer	Glassy Polymer Content % by wt	Modulus 300% kg/cm^2	Elongation at Break %	Tensile Strength kg/cm^2
PS	13	26.0	310	27.0
	27	56.0	315	57.0
	60	--	210	137.0
P-α-MeSt	50	158	325	164.0

Representative stress-strain curves are given in Figure 2. The graft polymers examined contained from 13 to 60 weight % glass (PS or P-α-MeSt) polymer.

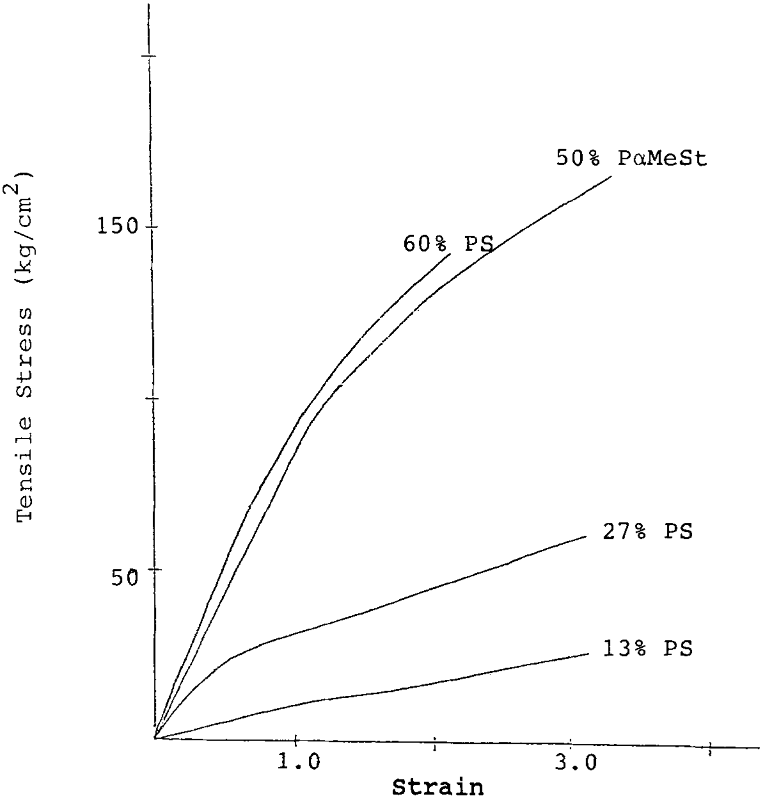

Figure 2
Stress-Strain Curves of the Graft Copolymers

As shown in Table III, the tensile strengths and the moduli increase with increasing glassy polymer content of the graft copolymers. Although the tensile strengths and the 300% modulus are high for all the samples which were tested, most of the specimens broke at rather low elongations. This might be due to some flaw in the films. It was interesting to note that the tensile properties of two graft copolymers, one containing 60% PS and the other 50% P-α--MeSt, are almost identical. A similar phenomenon was observed by Kennedy and Vidal (5) which was attributed to the higher Tg of P-α-MeSt (182 °C), than that of PS (100 °C). The stress-strain curves indicate that the graft polymers with higher glassy polymer content are tough plastics.

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