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Synthesis of a New EPM-Polystyrene Graft Terpolymer

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Summary

An EPDM graft terpolymer was prepared using the macromer polystyryldicyclopentadiene (PSt-DCp). Terpolymerization of PSt-DCp with ethylene and propylene led to a new material containing five branches per chain. The terpolymer was characterized by GPC, osmometric measurements, and NMR spectroscopy.

Introduction

Certain alkyl halides, e.g., t-butyl chloride, benzyl chloride, in conjunction with certain alkylaluminum compounds such as $(C_2H_5)_2AlCl$ initiate the cationic polymerization of a variety of olefins (1, 2, 3, 4). One of these initiators is 1-chlorodicyclopentadiene (DCp-Cl), which was used recently to initiate the polymerization of isobutylene to give polyisobutenyldicyclopentadiene (PIB-DCp) (5). Using the DCp-Cl initiator, we carried out the analogous polymerization of styrene to give PSt-DCp, a new macromer, which was then terpolymerized with ethylene and propylene to give a new EPDM-g-PSt. The new graft terpolymer consisted of the rubbery ethylene-propylene copolymer backbone carrying glassy polystyrene branches.

This paper is concerned with the preparation and characterization of a new polystyrene macromer, a method of incorporating the macromer onto an EPDM, and the characterization of the final EPDM-g-PSt.

Experimental

Materials. Anhydrous methylene chloride (Aldrich, Gold Label) was used as received. Reagent grade toluene (Fisher) was refluxed over calcium hydride and distilled under nitrogen. Spectrograde chloroform (Fisher) was used in the epoxidation titrations. 1,4-Dioxane was refluxed over $NaBH_4$ and then distilled. Anhydrous ether (Fisher) was refluxed over Na/benzophenone and distilled under N_2. Reagent grade solvents were used for solvent extractions and work up.

Dicyclopentadiene (Aldrich) was purified by vacuum distillation. Selenium dioxide and thionyl chloride (Aldrich) were used as received.

Diethylaluminum chloride (25.6% in heptane) and ethylaluminum sesquichloride (24.5% in heptane) were obtained from Texas Alkyls. In some cases they were used as received or purified for certain experiments by vacuum distillation of the heptane, followed by vacuum distillation of the alkylaluminum chlorides, then redissolving in purified heptane or other solvent. Vanadium oxychloride (Aldrich) was distilled under nitrogen and stored in flamed-out amber bottles in the refrigerator.

Reagent grade styrene was stirred under N_2 for 4 days and then dis-

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tilled under vacuum. m-Chloroperbenzoic acid (80-85%) was purified by washing successively with a phosphate buffer prepared from 67.1g of $Na_2HPO_4 \cdot 7H_2O$ and 34.0g KH_2PO_4 in 1L of distilled H_2O. This was suction filtered and extracted with a minimum amount of methylene chloride. The solvent was removed by a rotary evaporator and the recovered m-chloroperbenzoic acid was dried under vacuum at room temperature. It was stored under nitrogen in a refrigerator.

Physical Methods. ^1H NMR spectra were obtained on a Varian EM360 spectrometer using TMS as the internal standard. The molecular weights of the low molecular weight polymers were determined on a Knauer Vapor Pressure Osmometer using toluene at 45°C, whereas those of the high molecular weight polymers were determined on a Hewlett-Packard 503 high-speed membrane osmometer using toluene at 37°C. Waters 150-C GPC, equipped with dual detectors (UV and RI) and microstyrogel columns of 10^6, 10^5, 10^4, 10^3, 500 and 100 Å. Approximately 0.25% polymer solutions in THF were used at a flow rate of 1 mL/min. Elution counts were calibrated by polystyrene and polyisobutylene standards.

A Beckman Model J21-C centrifuge was used during selective solvent extractions to isolate the pure graft copolymer. The solutions were spun for 15-30 minutes at 0°C with a spin rate of 12,000 rpm.

Preparation of DCp-Cl. This compound was synthesized by the chlorination of DCp-OH according to Dilling et al. (6) The alcohol was prepared by allylic oxidation of DCp by SeO_2 (7).

Preparation of DCp-PSt. Polymerizations were carried out in clean, flamed out, serum-capped flasks in a glove box under a dry nitrogen atmosphere. A parallel control reaction duplicating the conditions of polymerization was carried out each time a polymerization reaction was performed to ensure that the system was essentially moisture free. In the control reaction the DCp-Cl was absent. In a typical experiment, 12 mL of CH_2Cl_2, 2.0 mL styrene and 5 mL of a 0.106 M DCp-Cl solution in CH_2Cl_2 were placed in the flask and the contents were cooled to -70°C in a hexane bath. When the system had reached equilibrium, 5mL of 0.575 M $(C_2H_5)_2AlCl$ solution in CH_2Cl_2 was injected into the flask and the reaction mixture was agitated manually. The polymerization was terminated after 5 minutes by injecting 5 mL precooled methanol into the flask. The reaction mixture was then added to 60 mL methanol, the precipitated polymer was collected by suction filtration and dissolved in chloroform. The solvent was removed on a rotary evaporator and the polymer was dried under a high vacuum at 50°C.

For subsequent studies, the polymer was purified further as follows. The PSt-DCp was dissolved in toluene and passed down a Florisil column several times. The solution was washed with aqueous sodium potassium tartrate solution and distilled water to remove any remaining aluminum oxides. Then the polymer was subjected to the cycle of dissolving in toluene and precipitating from methanol four times. The precipitated polymer was collected by filtration and dried under high vacuum.

Epoxidation Titrations. The method of Dreyfuss and Kennedy was used to estimate the number of DCp groups (number of double bonds) per mole of polymer (8). In a typical titration 0.2-0.5g of polymer was dissolved in 10 mL chloroform and 5 mL 0.12-0.13 peracid solution was added, along with aqueous KI and acetic acid. The liberated I_2 was back titrated with sodium thiosulfate solution.

Synthesis of EPDM-q-PSt. A 500 mL, 4-neck flask was dried in the oven and flamed out under N_2. Into the flask was placed 250 mL dry toluene and a magnetic stirrer. Rubber septums were placed on three necks and to the fourth was attached a pressure-equalized separatory funnel containing

50 mL of a toluene solution of DCp-PSt ($\bar{M}n$ = 10,240) at a concentration of 0.1g/mL. The solvent in the flask was saturated with ethylene and propylene gases for 15 minutes. Both gases were passed through columns containing CuO at 150°C to remove any H_2 and then through drierite columns to remove H_2O. The flow rate of each gas was monitored through flow meters at 1L/minute. The DCp-PSt solution was added dropwise over a period of 11 minutes. Simultaneously, the two catalyst components $(C_2H_5)_3Al_2Cl_3$ (0.12M in toluene) and $VOCl_3$ (0.03M in toluene) were added dropwise by means of a syringe pump at a rate of 1 mL/minute maintaining a 4:1 ratio of Al:V. At the end of the addition of the macromer, the additions of catalysts, ethylene, and propylene were terminated. The reaction mixture was stirred for 5 minutes and then poured into 600 mL acetone. The precipitated polymer was collected by decantation and the turbid acetone solution was centrifuged to recover the remaining polymer. The combined polymer was dissolved in toluene and reprecipitated in acetone to dissolve any unreacted DCp-PSt. The insoluble polymer was extracted with heptane to dissolve ethylene-propylene copolymer (EP). This extraction was repeated until all EP polymer was removed. The material that is insoluble in both acetone and heptane is the graft terpolymer. The material was collected and dried under vacuum. The ^1H NMR spectrum (CS_2 solution) of the graft polymer showed aromatic proton signals from polystyrene and aliphatic signals from the ethylene-propylene backbone. The compound was further characterized by membrane osmometry and GPC.

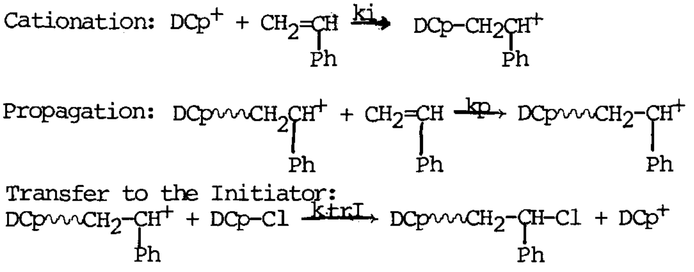
The graft terpolymer was also prepared by placing the macromer in 225 mL toluene and then adding the other monomers and catalysts. The graft terpolymer was obtained in slightly increased yields over the first method.

Results and Discussion

Recently Farona and Kennedy reported the synthesis of a new graft EPDM terpolymer, made from the reaction of the macromer DCp-PIB with ethylene and propylene (9). One of the objectives of this research was to synthesize a glassy polymer with a desirable head group in order to incorporate it into an EPDM polymer. To this end, we prepared polystyrene attached to a DCp head group and used this macromer as the diene in the terpolymerization with ethylene and propylene.

Following is the anticipated reaction scheme for styrene polymerization by the DCp-Cl/$(C_2H_5)_2AlCl$ initiator.

Ion Generation: $DCp\text{-}Cl + R_2AlCl \rightleftarrows DCp^+ + R_2AlCl_2^-$

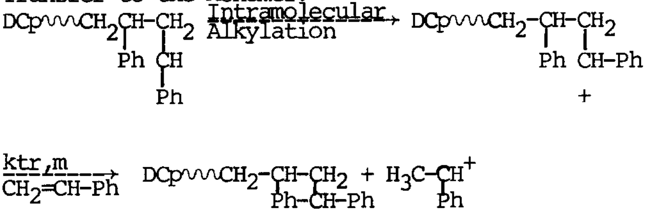


Cationation: $DCp^+ + CH_2{=}\underset{Ph}{CH} \xrightarrow{ki} DCp\text{-}CH_2\underset{Ph}{CH^+}$

Propagation: $DCp\sim\sim CH_2\underset{Ph}{CH^+} + CH_2{=}\underset{Ph}{CH} \xrightarrow{kp} DCp\sim\sim CH_2\text{-}\underset{Ph}{CH^+}$

Transfer to the Initiator:
$DCp\sim\sim CH_2\text{-}\underset{Ph}{CH^+} + DCp\text{-}Cl \xrightarrow{ktrI} DCp\sim\sim CH_2\text{-}\underset{Ph}{CH}\text{-}Cl + DCp^+$

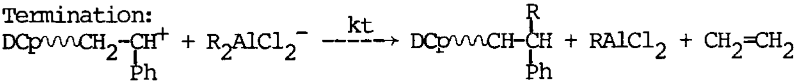
Transfer to the Monomer:



$$\mathrm{DCp{\sim\sim}CH_2\underset{Ph}{CH}-\underset{\underset{Ph}{CH}}{CH_2}} \xrightarrow[\text{Alkylation}]{\text{Intramolecular}} \mathrm{DCp{\sim\sim}CH_2-\underset{Ph}{CH}-\underset{CH-Ph}{CH_2}} +$$

$$\xrightarrow[\mathrm{CH_2=CH-Ph}]{k_{tr,m}} \mathrm{DCp{\sim\sim}CH_2-\underset{Ph-CH-Ph}{CH-CH_2}} + \mathrm{H_3C-\underset{Ph}{CH^+}}$$

Termination:



$$\mathrm{DCp{\sim\sim}CH_2-\underset{Ph}{CH^+}} + \mathrm{R_2AlCl_2^-} \xrightarrow{kt} \mathrm{DCp{\sim\sim}CH-\overset{R}{\underset{Ph}{CH}}} + \mathrm{RAlCl_2} + \mathrm{CH_2=CH_2}$$

The nature of the polymer head group is determined by the relative rates of cationation and chain transfer to monomer. The DCp head group is formed only during initiation. Chain transfer to monomer results in a sterile methyl group rather than the desired DCp head group. The growing polystyrene chain is believed to undergo chain transfer to monomer by intramolecular penultimate alkylation (10, 11). Kennedy and co-workers observed chain transfer to monomer during their attempt to synthesize poly(isobutylene-b-styrene) by cationic polymerization (12).

For a DCp-headed polymer to form quantitatively, ktr,m must be zero. We believe that, under the conditions employed for the polymerization of styrene, i.e., high DCp-Cl concentration and low temperature, chain transfer to monomer will be negligible.

A series of polymerization studies were carried out to determine ktr,m. The data are shown in Table 1.

Table 1. Experimental Data to Determine the Value of ktr,m*

Expt	[M]	[DCp-Cl]	[ET$_2$AlCl]	Conversion** %	$\overline{\mathrm{Mn}}$ by VPO
1	0.821M	------	1.23×10^{-1}M	2.5	--
2	0.821M	2.26×10^{-2}M	1.23×10^{-1}M	100	6,700
3	0.671M	2.26×10^{-2}M	1.23×10^{-1}M	100	5,300
4	0.572M	2.26×10^{-2}M	1.23×10^{-1}M	100	5,000
5	0.372M	2.26×10^{-2}M	1.23×10^{-1}M	100	3,000

*Solvent=CH$_2$Cl$_2$; Time=5 minutes; Temperature=70°C; Total Volume-23.4mL Exp. 1 is the control (no DCpCl). **Determined by weight of polymer. Values are approximate.

A plot of 1/Dp$_n$ vs. 1/[M] gives a straight line which passes through the origin, indicating that there is no chain transfer to the monomer to a measurable extent. This is shown in Figure 1.

Since ktr,m appears to be zero, every polymer molecule must be headed by a DCp group. This can be verified by epoxidation titration of the number of double bonds in a polymer (8). DCp itself was used as the model olefin to show a quantitative reaction with m-chloroperbenzoic acid in a short reaction time. This was accomplished by carrying out the reaction in NMR tubes and recording the spectrum immediately. Olefinic signals were absent immediately after mixing the reactants. The data are shown in Tables 1 and 2.

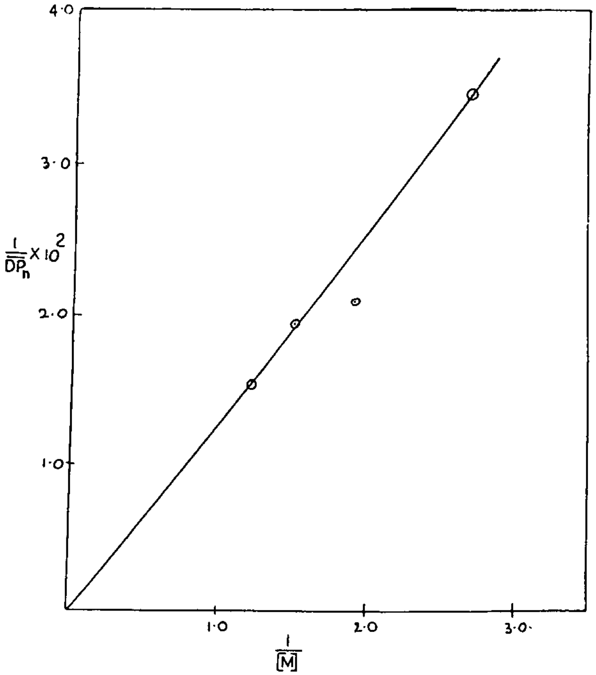


Figure 1. Plot of $1/Dp_n$ vs. $1/[m]$

Table 2. Titration of DCp by m-Chloroperbenzoic Acid

g DCp	mol DCp	moles of db from titration	moles db/ mole DCp	Theoretical Value
0.0495	3.744×10^{-4}	7.6×10^{-4}	2.0299	2.0
0.0283	2.141×10^{-4}	4.3×10^{-4}	2.008	2.0

For the above titrations, 10 mL of $CHCl_3$ was used as the solvent and 5 mL of 0.3188M solution of m-CPBA in $CHCl_3$ was added to the titration mixture.

Table 3. Titration of DCp-PSt by m-Chloroperbenzoic Acid

$\overline{Mn}$	% of polymer	mole of Polymer$\times10^5$	mole of db $\times 10^5$	mole db/ mole polymer	Theoretical Value
10,240	0.251[a]	2.45	5.0	2.04	2.0
	0.499][b]	4.88	10	2.049	2.0
	0.3491[b]	3.41	8.0	2.3	2.0
13,650	0.20[c]	1.47	3.0	2.041	2.0

10 mL of $CHCl_3$ was used for each titration

a. 5 mL of 0.1298M solution of m-CPBA was used

b. 5 mL of 0.1241M solution of m-CPBA was used

c. 5 mL of 0.0475M solution of m-CPBA was used

From the data in Tables 2 and 3 it is evident that there is exactly one DCp group attached to every polymer chain.

Attempts were made to prepare two DCp-PSt macromers: one of $\overline{M}_n$=10,000 and one of $\overline{M}_n$ =20,000. According to the $1/Dp_n$ vs. 1/[M] plot, it was necessary to use [styrene]=1.25M for the lower and 2.5M for the higher molecular weights at [DCp-Cl]=2.26×10^{-2}M. The samples prepared showed $\overline{M}_n$s of 10,240 and 16,900 by GPC.

Figure 2 shows a typical GPC curve of the graft terpolymer. The branches/backbone (b/B) ratio was calculated from molecular weight studies and NMR spectrometry. The proton NMR spectrum is shown in Figure 3.

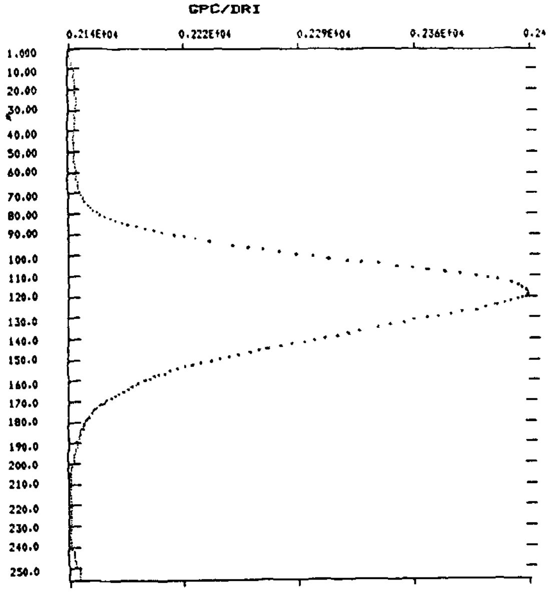


Figure 2. GPC Curve of EPDM-g-PSt

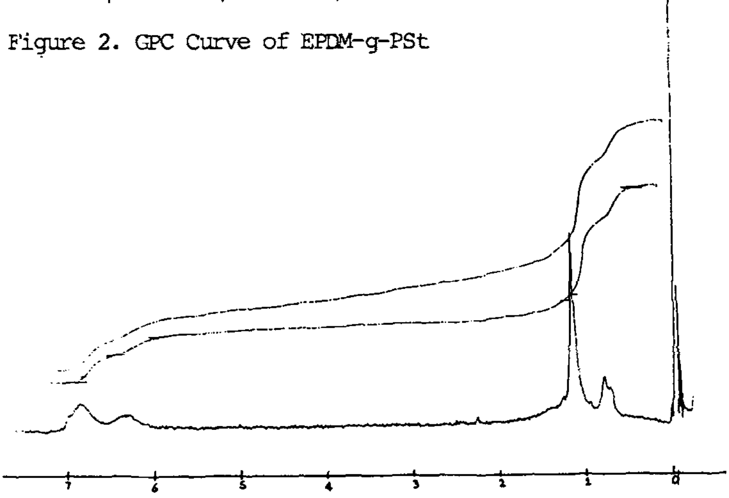


Figure 3. ^1H NMR Spectrum of EPDM-g-PSt

The graft terpolymer synthesized using the DCp-PSt macromer of $\overline{Mn}$=10,240 showed a single, narrow and symmetrical peak by GPC with $\overline{Mn}$=80,000 (membrane osmometry). With respect to the $\overline{Mn}$ of the graft polymer and integration of the proton signals in the NMR spectrum, there are five polystyrene branches along the EPDM backbone. Molecular weight studies indicate a PSt/EP ratio of 63/37, while the proton signal integration studies show PSt/EP of 65/35. Previous work done in this area led to low (∿1.0) b/B ratios (9, 14).

The original synthetic method for terpolymerization was modified slightly in an attempt to improve the yield. Thus, a DCp-PSt macromer of $\overline{Mn}$=16,900 was dissolved in CH_2Cl_2 and placed in the reaction flask, rather than added dropwise. The resulting graft polymer showed a $\overline{Mn}$ = 58,500 and two polystyrene branches per EPDM backbone. It showed PSt/EP ratios of 58/42 and 55/45 by integration of the proton NMR signals. Evidently the yield has not significantly increased.

In conclusion, the data presented in this paper clearly show that a new polystyrene macromer, DCp-PSt, can be conveniently prepared by cationic polymerization using DCp-Cl/Et_2 AlCl at -70°C. The yields are very high and the DCp head group can be incorporated quantitatively--chain transfer to the monomer is absent under the conditions employed.

A graft copolymer consisting of a rubbery ethylene-propylene random copolymer backbone and glassy polystyrene branches can be successfully prepared by terpolymerizing ethylene propylene along with the DCp-PSt macromer, using conventional Ziegle-Natta catalysts. The number of polystyrene branches per backbone can be controlled by changing the concentration of the macromer. The graft terpolymer (EPDM-g-PSt) is expected to behave as a thermoplastic elastomer.

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