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Synthesis of an EPDM graft terpolymer

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Summary

An EPDM graft terpolymer was prepared using the macromer poly-α-methylstyryldicyclopentadiene (P-αMSt-DCp) as the diene with ethylene and propylene. The new material was characterized by GPC, osmometry, nmr spectrometry, and TGA measurements. Number average molecular weights are in the 24,000-29,000 range, and the polymer carries two branches per chain.

Introduction

1-Chlorodicyclopentadiene can be used to initiate cationic polymerization of certain monomers, e.g., isobutylene, employing such alkylaluminum halides as $(C_2H_5)_2AlCl$, as coinitiators. We have prepared macromers of polyisobutylene and polystyrene containing dicyclopentadiene as the head group, and then incorporated these macromers into EPDM polymers, thus producing EPDM graft terpolymers of polyisobutylene and polystyrene (1,2). We have now extended this work to include graft EPDM terpolymers of poly-α-methylstyrene.

Experimental

The preparation and purification of starting materials and solvents was the same as those employed in the synthesis of EPDM-g-PSt, as were the physical methods (2). TGA curves were taken on a Dupont 1090 Thermal Gravimetric Analyzer. DCp-Cl was prepared by the chlorination of DCp-OH according to the method of Dilling et al. (3)

The synthesis of P-αMSt-DCp was carried out in a manner analogous to that of PSt-DCp. The purification of the macromer for quantitative studies was effected as follows. The P-αMSt-DCp was dissolved in toluene and chromatographed on a Florisil column several times. The solution was washed with aqueous sodium potassium tartrate solution and distilled water to remove any remaining aluminum compounds. The polymer was then dissolved in toluene and precipitated from methanol; the process of dissolving and precipitating was repeated four times. The pure macromer was collected by filtration and dried under high vacuum.

The number of DCp head groups (number of double bonds) was determined by epoxidation titrations according to the method of Dreyfuss and Kennedy (4). In a typical titration, 0.2-0.5 g of the macromer was dissolved in 10 mL chloroform and 5 mL of 0.3188M m-chloroperbenzoic acid solution in $CHCl_3$ was added, along with aqueous KI and acetic acid. The liberated I_2 was back titrated with a standard sodium thiosulfate solution. The results of the titrations are shown below in Table 1 (db = double bond).

TABLE 1

Titration of P-αMSt-DCp by m-Chloroperbenzoic Acid

$\overline{Mn}$	g of Macromer	Mole of Polymer X10^5	Moles of db X10^5	Mole db/ Mole Macromer	Theoretical Value
6,550	0.25	3.82	8.0	2.09	2.0
	0.50	7.63	15.0	1.97	2.0
5,406	0.3	5.55	11.0	1.98	2.0
	0.45	8.32	15.0	1.80	2.0
4,055	0.20	4.93	10.0	2.03	2.0
	0.40	9.86	21.0	2.13	2.0

Synthesis of EPDM-g-P-αMSt. The preparation of the graft polymer was carried out in a manner analogous to that described for EPDM-g-PSt. At the time of precipitation of the polymer from the synthesis flask, the solid was composed of unreacted macromer, ethylene-propylene copolymer (EP), and the graft terpolymer. The combined polymer was dissolved in toluene and precipated in methanol. Methylethyl ketone (MEK) was found to be an excellent solvent for the macromer. The crude polymer was stirred with MEK for 24 hr. The insoluble polymer was isolated by decantation and centrifugation, and then stirred with heptane for several hours to remove soluble EP copolymer. The polymer that is insoluble in both MEK and heptane is the graft terpolymer. The compound was characterized by ^1H nmr, membrane osmometry, GPC, and TGA measurements.

Results and Discussion

In the report on the synthesis of EPDM-g-PSt, an anticipated reaction scheme was proposed for the styrene polymerization by DCp-Cl/$(C_2H_5)_2$ AlCl initiator (2). An analogous scheme exists for the polymerization of α-methylstyrene by the same initiator. One of the steps is a possible chain transfer to the monomer by intramolecular alkylation. In order to determine whether each P-αMSt chain bears a DCp head group, a series of polymerization studies was carried out to determine $k_{tr,m}$. The value of $k_{tr,m}$ must be zero for a DCp-headed polymer to form quantitatively. Table 2 displays the data of the polymerization studies, and Figure 1 shows a plot of $1/DP_n$ vs. $1/[M]$.

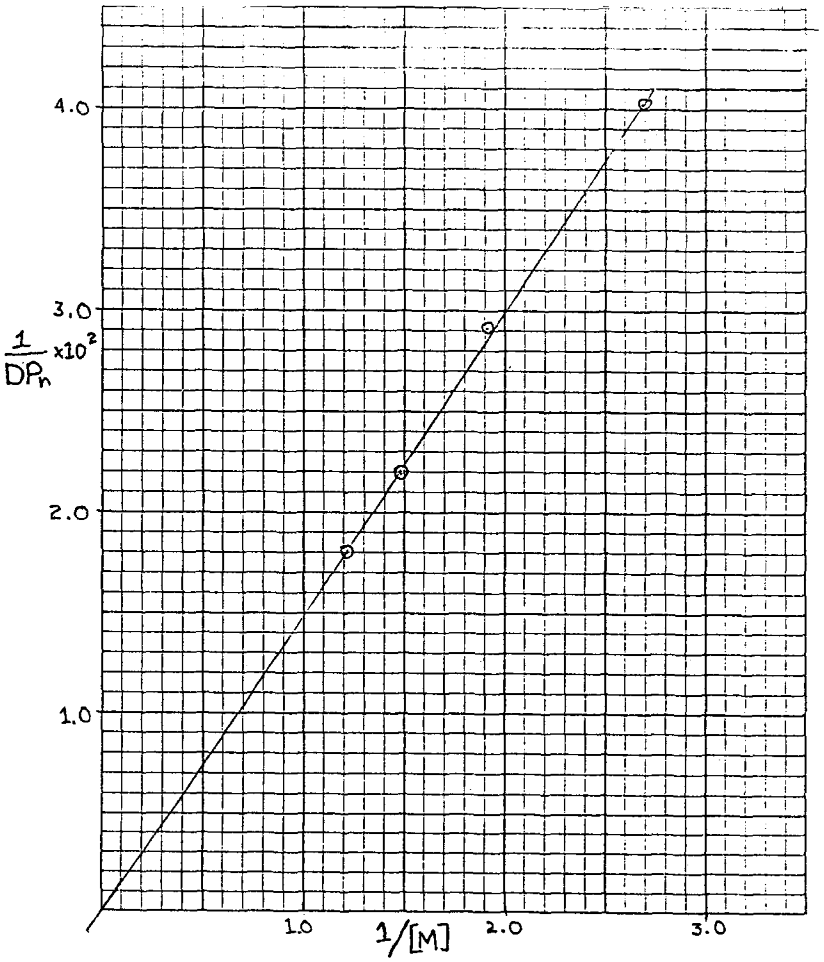
TABLE 2

Experimental Data to Determine the Value of $k_{tr,m}$*

Exp.	[M]	$\overline{Mn}$ by VPO	$\overline{DP}_n$	$1/DP_n x10^2$	1/[M]
1	0.821M	6550	55.42	1.80	1.22
2	0.671M	5400	45.74	2.19	1.49
3	0.522M	4050	34.31	2.92	1.92
4	0.372M	2940	24.84	4.03	2.69

*Solvent = CH_2Cl_2; time = 2 min.; temp. = -66°C;
[DCp-Cl] = $2.99x10^{-2}$M; [Et_2AlCl] = $1.44x10^{-1}$M;
[Et_2AlCl]/[DCp-Cl] = 4.8

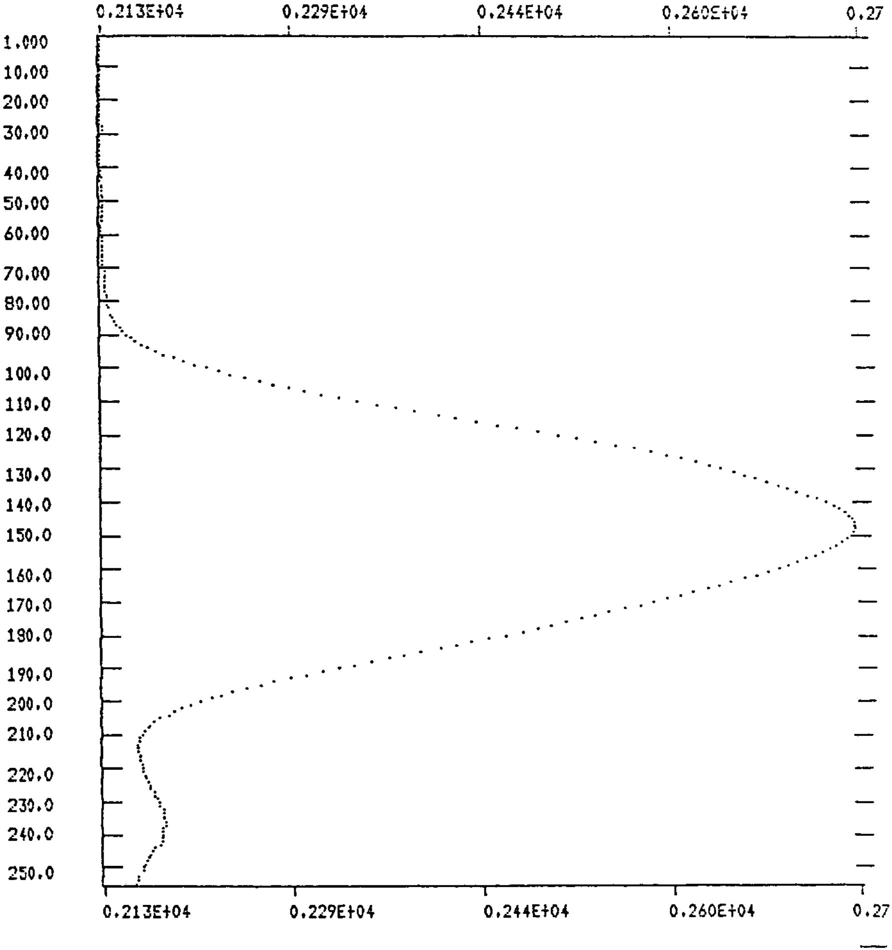
Figure 1 - Plot of 1/Dpn vs. 1/[M]



It is seen from Figure 1 that the plot of $1/DP_n$ vs. $1/[M]$ gives a straight line that passes through the origin, indicating that there is no chain transfer to the monomer under the conditions employed. Furthermore, the epoxidation titrations clearly show two double bonds per polymer chain, indicating that every chain is headed by one DCp group.

Figure 2 shows a typical GPC trace of the graft terpolymer. The number of branches per backbone ratio was calculated from molecular weight studies and nmr spectrometry.

Figure 2 - GPC curve of EPDM-g-P-αMSt

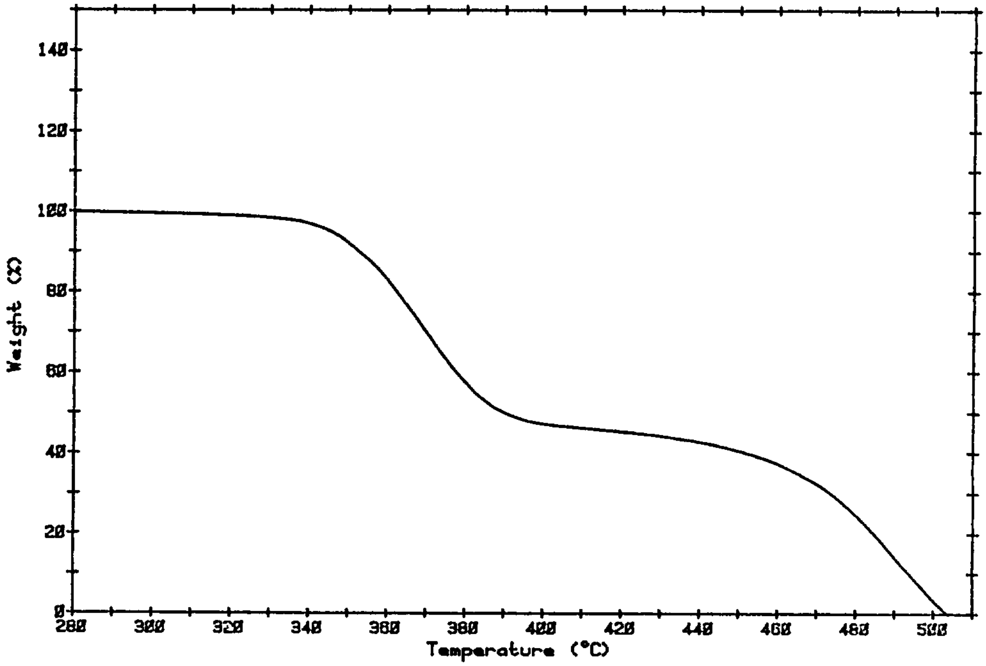


The macromer used in these studies demonstrated a $\overline{Mn}$ of 7,500 (64 monomer units) by membrane osmometry, while EPDM-g-P-αMSt showed a $\overline{Mn}$ of 29,200. The GPC curve of the terpolymer (Figure 2) showed a single, rather narrow, symmetrical peak with a polydispersity of 2.8.

The ^{1}H nmr spectrum exhibits an integrated intensity ratio of aromatic to EP protons of 5:13 or 1:2.6. Consequently, the average molecular weight of the EP backbone is 14,200, and using the data of $\overline{Mn}$ and nmr integrated intensities of EPDM-g-P-αMSt, it is calculated that the terpolymer contains an average of 2.2 branches per chain. The composition of the terpolymer is 51% P-αMSt and 49% EP.

TGA studies on the terpolymer show a weight loss (degradation) starting at 340°C, and a second weight loss starting around 450°(Figure 3). A TGA study of the macromer, P-αMSt-DCp, showed a single weight loss starting at 340° C. Therefore, the terpolymer, EPDM-g-P-αMSt, degrades first at the P-αMSt branches.

Figure 3 - TGA Curve of EPDM-g-P-αMSt



The data show that a new macromer, P-αMSt-DCp, can be prepared conveniently at low temperatures by cationic polymerization. The yields are high and chain transfer to the monomer is essentially non-existent.

A graft EPDM terpolymer consisting of the elastomeric ethylene-propylene backbone and glassy poly-α-methylstyrene branches can be prepared, using the macromer as the diene, with conventional Ziegler-Natta catalysts. Like EPDM-g-Pst, the graft terpolymer prepared in this work is expected to behave as a thermoplastic elastomer.

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