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Anionic Graft Copolymers. II.
Styrene Grafts on EPT Rubbers

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ABSTRACT

Rubbers containing a low level of unsaturation such as EPT may be metalated with a chelate made from s-butyllithium and N,N,N',N'-tetramethylethylenediamine. The lithiated polymers, reacted with styrene, result in polystyrene graft copolymers. The physical properties are affected by graft level and polystyrene content.

Papers by Langer and Eberhard [1] describing chelated organolithium compounds served as a stimulus for many investigations of the reactions of these compounds. Langer and Eberhardt found that hydrogen abstraction occurred with compounds such as benzene, toluene, and alkenes. Gosnell et al. [2] examined the reaction of chelated organolithiums with poly(2-vinylpyridine) and subsequent reaction of this polylithiated species with styrene and isoprene. Graft polymers of polystyrene and polyisoprene on poly(2-vinylpyridine) resulted. Minoura et al. [3] metalated polybutadiene and polyisoprene with an organolithium chelate made from n-butyllithium and N,N,N',N'-tetramethylethylenediamine. Graft polymers resulted when the

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polylithiated diene was reacted with vinyl aromatics such as styrene. Many other investigators have studied the metalation of polydienes [4].

Few instances of metalation of polymers containing low levels of unsaturation have appeared in the literature. Halasa and Tate [5] metalated an ethylene, propylene terpolymer, Nordel 1040, with a n-butyllithium N,N,N',N'-tetramethylethylenediamine chelate. Metalation was indicated by formation of the carboxyl and trimethylsilyl derivatives by reacting the lithiated polymer with carbon dioxide and trimethylsilyl chloride.

This paper describes the reaction of rubbers containing a low level of unsaturation with the chelate made from s-butyllithium and N,N,N',N'-tetramethylethylenediamine. We have found that this organolithium chelate is superior to the n-butyllithium N,N,N',N'-tetramethylethylenediamine chelate usually employed, in that more complete and facile lithiation is achieved [6]. The lithiated polymers, reacted with styrene, result in polystyrene graft copolymers. The properties of these were compared with respect to graft level and polystyrene content.

RESULTS AND DISCUSSION

The commercial rubbers employed in this work were dissolved in cyclohexane, filtered to remove gel, and washed with dilute nitric acid and water to remove catalyst impurities and stabilizers which might interfere with metalation reactions. Precipitation in isopropanol was followed by drying at 60°C under vacuum.

The purified rubber was redissolved in cyclohexane. N,N,N',N'-tetramethylethylenediamine was added followed by the requisite amount of s-butyllithium. The solution was stirred at room temperature for 2 hr. Styrene was added and the typical yellow color of living polystyrene appeared within a few minutes. The reaction mixture was stirred at 50°C for 16 hr. The yellow color of living polystyrene was titrated to colorless with a known amount of isopropanol. The efficiency of polystyrene grafting was determined by acetone extraction:

$$\text{graft efficiency } (\%) = \frac{\begin{pmatrix}\text{total wt of styrene}\\ \text{polymerized}\end{pmatrix} - \begin{pmatrix}\text{wt of polystyrene}\\ \text{acetone extracted}\end{pmatrix}}{\text{total wt of styrene polymerized}}$$

Polystyrene grafting on an amorphous ethylene, propylene terpolymer containing a small amount of a nonconjugated diene, Enjay 4504, is described in Table 1.

At a low level of metalation, 0.017 mmole of s-butyllithium per gram of rubber, Entry 1, a graft efficiency of 98% occurs. Polymers containing 50% styrene were examined. As expected, an increase in the level of

TABLE 1. Polystyrene Grafting on Enjay 4504[a]

Entry	Type[b]	mm SBL[c] / g R	% Graft efficiency	η_{sp}/c[d]	Tensile strength (psi)		% Elongation
					Yield	Ultimate	
1	50S-R	0.017	98	0.81	370	270	100
2	50S-R	0.035	92	0.75	480	470	80
3	50S-R	0.052	66	0.73	70	420	110
4	50S-R	0.067	10	0.68	Too soft to test		
5	30S-R	0.009	98	0.90	-	150	1450
6	70S-R	0.009	77	0.63	-	1900	<5

[a] Purified; η_{sp}/c = 1.1, 0.1 g/dl in benzene at 25°C.

[b] S = styrene; R = rubber (Enjay 4504); 50% styrene polymer was prepared.

[c] SBL = s-butyllithium; R = Enjay 4504.

[d] 0.1 g/dl in benzene at 25°C.

s-butyllithium causes a decrease in graft efficiency, Entries 3 and 4. Allylic sites are rapidly quantitatively metalated. Any excess of s-butyllithium leads to the formation of homopolystyrene, thus leading to a decrease in graft efficiency. At a styrene level of 30%, high graft efficiency occurs, Entry 5, while at a styrene level of 70%, Entry 6, a low graft efficiency is noted. This may reflect solubilization of part of the rubber phase by the long polystyrene chain attached to it. Irrespective of the s-butyllithium level used for metalation, and hence the graft efficiency and the percent styrene in the final product, low tensile products result. They are only slightly stronger than the substrate rubber which is too weak to test.

Metalated Enjay 4504 was reacted with trimethylsilyl chloride. Elemental analysis showed silicon incorporation, thus confirming anion formation on the rubber.

The metalation and subsequent polystyrene grafting on another ethylene, propylene terpolymer containing a small amount of a nonconjugated diene, Nordel 1070, is described in Table 2. The results are similar to the Enjay 4504 study. At a low level of s-butyllithium, 0.024 mmole per gram of rubber, Entry 1, high graft efficiency results. As the s-butyllithium level is increased graft efficiency falls off, Entries 2 through 4, indicating a lower level of labile allylic hydrogens than in Enjay 4504; compare with Entires 1 to 3 in Table 1. Polystyrene

TABLE 2. Polystyrene Grafting on Nordel 1070[a]

Entry	Type[b]	mm SBL[c] g R	% Graft efficiency	η_{sp}/c[d]	Tensile strength (psi) Yield	Tensile strength (psi) Ultimate	% Elongation
1	50S-R	0.024	84	0.88	410	300	160
2	50S-R	0.070	68	0.81	300	240	280
3	50S-R	0.13	66	0.88	260	240	130
4	50S-R	0.22	58	0.86	250	220	120
5	10S-R	0.030	86	1.44	90	90	2900
6	70S-R	0.037	95	0.73	-	1580	<5

[a] Purified; $\eta_{sp}/c = 1.50$, 0.1 g/dl in benzene at 25°C.

[b] S = styrene; R = rubber (Nordel 1070); 50% styrene polymer was prepared.

[c] SBL = s-butyllithium, R = rubber.

[d] 0.1 g/dl in benzene at 25°C.

grafts containing high and low levels of styrene are prepared with high graft efficiencies, Entries 5 and 6. The polymers described in Table 2 are low tensile strength materials, slightly tougher than virgin Nordel 1070 which is too weak to test.

Several other rubbers which have low levels of unsaturation may be employed as substrates in metalation reactions, Table 3. Ethylene, propylene terpolymers containing a small amount of a nonconjugated diene, Enjay 3509 and Nordel 1145, may be metalated with a s-butyllithium N,N,N',N'-tetramethylethylenediamine chelate and grafted at a 50% level with polystyrene. High graft efficiencies resulted, but the products were low in tensile strength.

Enjay 404 ethylene, propylene rubber, and Enjay 325 butyl rubber are materials containing very few active sites for metalation, Entries 3 and 4. Nevertheless, these polymers may be metalated with the s-butyllithium N,N,N',N'-tetramethylethylenediamine chelate and grafted with polystyrene. The graft efficiencies are low, 57 and 52%, respectively, but in all probability could be increased to near 100% by using a lower level of s-butyllithium N,N,N',N'-tetramethylethylenediamine chelate. Low tensile strength materials result.

A slurry of polyethylene and cyclohexane may be reacted with the s-butyllithium N,N,N',N'-tetramethylethylenediamine chelate, Entry 5. Addition of styrene results in its polymerization. Acetone extraction

TABLE 3. Polystyrene Grafting on Some Rubbers[a]

Entry	Substrate	mm SBL[b] / g Substrate	% Graft Effic	η_{sp}/c[c]	Tensile strength (psi) Yield	Tensile strength (psi) Ultimate	% Elongation
1	Enjay EPT 3509	0.05	84	0.95	330	390	60
2	Nordel EPT 1145	0.078	80	0.74	390	300	260
3	Enjay EPR 404	0.065	57	0.86	Too weak to test		
4	Enjay Butyl 325	0.045	52	0.46	650	680	33
5	Eastman Polyethylene 2630F	0.185	Infrared showed styrene incorporation				

[a] 50% styrene containing polymers.

[b] SBL = s-butyllithium.

[c] 0.1 g/dl in benzene at 25°C.

of the precipitated material removes most of the polystyrene; however, the IR spectrum of the insoluble portion shows a trace of polystyrene, thus indicating a small amount of polystyrene grafting and hence metalation.

Thus rubbery materials such as EPR which contain very low levels of unsaturation can be readily metalated by treatment with s-butyllithium N,N,N',N'-tetramethylethylenediamine chelates. Where the level of active chelate does not exceed the availability of reactive sites, the metalation is highly efficient and the resulting metalated substrates give graft copolymers with styrene in high yield. The physical properties of these graft copolymers generally were those of low strength gum stocks.

EXPERIMENTAL

The rubbers were dissolved in cyclohexane, filtered to remove gel, and washed with dilute nitric acid and water to remove catalyst impurities and stabilizers. Precipitation in isopropanol was followed by drying at 60°C in vacuum.

Purified Enjay 4504, $\eta_{sp}/c = 1.0$ in benzene at 25°C, 10.0 g was dissolved in 700 ml of cyclohexane which had been passed over molecular sieves. The solution was degassed with dry nitrogen. Dry, freshly distilled N,N,N',N'-tetramethylethylenediamine, 0.51 mmole, was added. s-Butyllithium, 0.51 mmole, was added and the mixture was stirred at room temperature for 2 hr. Freshly distilled styrene, 10.0 g, was added and the reaction mixture was stirred at 50°C for 16 hr. The characteristic yellow color of living polystyrene was titrated to colorless with 0.34 mmole of isopropanol. The polymer was precipitated in isopropanol and dried at 60°C under vacuum. The other polymers investigated in this paper were metalated and grafted with polystyrene in a similar manner.

Graft efficiency was determined by extracting a 1.5-g sample with acetone in a Soxhlet extraction apparatus until the soluble polystyrene had been removed.

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REFERENCES

[1] A. W. Langer, Trans. N. Y. Acad. Sci., Ser. II, 27, 741 (1965). G. G. Eberhardt and W. A. Butte, J. Org. Chem., 29, 2928 (1964).

[2] A. B. Gosnell, J. A. Gervasi, D. K. Woods, and V. Stannett, J. Polym. Sci., C, 22, 611 (1969).

[3] Y. Minoura and H. Harada, Ibid., A-1, 7, 3 (1969); H. Harada, K. Shiina, and Y. Minoura, Ibid., A-1, 6, 559 (1968).

[4] G. Vaughan and G. A. Pope, South Africa Patent 682,597 (April 26, 1967); British Patent 1,173,508 (December 10, 1969); W. A. Butte, Belgian Patent 698,822 (May 22, 1969); F. E. Naylor, U.S. Patent 3,492,369 (January 27, 1970); and R. J. Schlott and J. C. Falk, Unpublished Results.

[5] A. F. Halasa and P. P. Tate, South African Patent 677,680 (December 8, 1967).

[6] R. J. Schlott and J. C. Falk, Unpublished Results.

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