Notes

Dilithium Anionic Initiators Based on Double 1,1-Diphenylethylene Compounds

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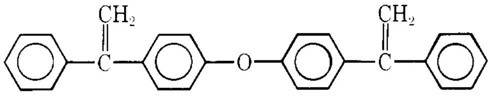
Triblock copolymers containing a polydiene as the center block are important thermoplastic elastomers. Commercially they are made by anionic polymerization using butyllithium initiators.[1] To assure the optimum polydiene microstructure for good elastomeric properties, pure hydrocarbon solvents are used in all phases of the polymerization. Many monomers requiring polar solvents or additives for polymerization cannot be conveniently used in such processes. This restriction is removed if a dilithium initiator is used to polymerize first the center polydiene block. For example, Fetters and Morton[2] prepared poly(α-methylstyrene–isoprene–α-methylstyrene), also, Morton and Mikesell[3] prepared poly(ethylene sulfide–diene–ethylene sulfide) by such a route. The initiator used by them was 1,4-dilithio-1,1,4,4-tetraphenylbutane which was prepared by the reaction of 1,1-diphenylethylene with lithium dispersion in a hydrocarbon solvent containing 15% anisole. The amount of anisole present was shown to give no ill effect on the microstructure of the polydiene block. Other known dilithium initiators are formed by the reaction of metallic lithium with an aromatic hydrocarbon[4] or by the addition reaction of *sec*-butyllithium with divinylbenzene[5] or diisopropenylbenzene[6] in hydrocarbon solvents. The last preparative route appears to be the simplest. More recently Foss, Jacobson, and Sharkey[7] prepared an initiator by reacting *sec*-butyllithium with *m*-diisopropenylbenzene in cyclohexane containing a small amount of triethylamine as an additive.

It has been reported[8,9] that butyllithium adds readily to 1,1-diphenylethylene (1,1-DPE) in hydrocarbon solvents. The product can initiate isoprene and butadiene to form copolymers with 1,1-DPE but because of the bulkiness of the phenyl groups 1,1-DPE does not homopolymerize. It appears then the addition of butyllithium to compounds containing two 1,1-diphenylethylene groups should produce useful dilithium initiators. We have prepared four such double 1,1-DPE compounds:



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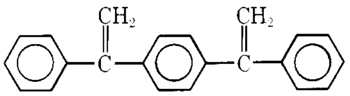

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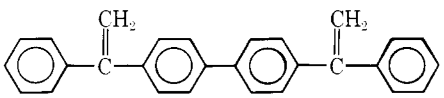

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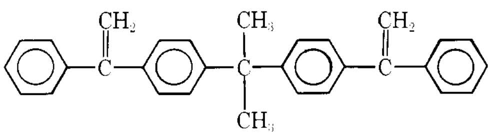

IV

Compound I, bis[4-(1-phenylethenyl)phenyl] ether, and compound III, 4,4′-bis(1-phenylethenyl)-1,1′-biphenyl, have been reported by Neville and Rosser.[10,11] Compound II, 1,4-bis(1-phenylethenyl)benzene, has been reported by Hacker and Lattermann.[12] All three compounds are solids with defined melting points. Compound IV, 2,2-bis[4-(1-phenylethenyl)phenyl]propane, apparently has not been reported before. It was prepared by the same methods except that 2,2-diphenylpropane was used as the starting material. The product was a viscous liquid and was difficult to purify. The final form was about 90% pure by GC chromatography and was brownish colored. Spectra of infrared and NMR for the product were consistent with the structure of compound IV.

Table I
Gelation Tests for Difunctional Anions

Initiator		Butadiene, g	$SiCl_4$, mequiv	% gel	
Type	mequiv			Obsd	Theory
s-BuLi + compd I	3.24	57	2.09	56.6	65.0
s-BuLi + compd II	1.67	50	1.12	55.3	67.0
s-BuLi + compd III	2.82	38	2.44	60.0	86.0
s-BuLi + compd IV	4.30	35	2.79	>90.0	
s-BuLi	1.45	52	1.22	None	None

The reaction of *sec*-butyllithium with the double 1,1-DPE compounds was conducted in a 100-mL round-bottom flask equipped with a rubber-septum-capped side arm. The flask was dried and flushed with dried prepurified nitrogen before use. Stirring was done magnetically. No heating except that derived from the magnetic stirring motor was supplied. The double 1,1-DPE compounds were used in concentrations about 0.03 M in benzene. A 5% excess of *sec*-butyllithium was used to counteract the estimated amount of impurities still existing in the system. Upon the addition of *sec*-butyllithium the reaction mixture turned immediately to a very deep color. For compound I, the color was deep red; for compound II, the color was deep purplish red; for compound III the color was deep blue; and for compound IV the color was deep brownish red. Solids in fine dispersion form appeared a few minutes thereafter. The addition reaction was completed in about 3 h as indicated by infrared spectroscopy and GPC chromatography of the product after treatment with glacial acetic acid.

The fine dispersion formed for all four double 1,1-DPE compounds was found to initiate the polymerization of 1,3-butadiene. The difunctionality of the initiators was demonstrated by a gelation test described by Farrar.[6] The procedure used by us for the polymerization and gelation was as follows:

The initiator dispersion was introduced dropwise into a nitrogen-purged 1-L reaction flask containing approximately 450 mL of degased dry benzene and 7 g of 1,3-butadiene. After the initiator color persisted upon the dropping of the dispersion, the rest of the dispersion was added quickly. The solution was then warmed to 45 °C using an external water bath. Thirty minutes later all solid dispersion became dissolved. More butadiene monomer was then added and the polymerization was completed in about an hour at 45 to 55 °C. Two milliliters of freshly distilled tetrahydrofuran was added together with a 0.9 M $SiCl_4$ in benzene solution. Visible gels formed immediately. Table I summarizes the results.

The initiator derived from compound I was used to prepare two poly(styrene–butadiene–styrene) triblock copolymers to further test its efficacy as a difunctional initiator. The buta-

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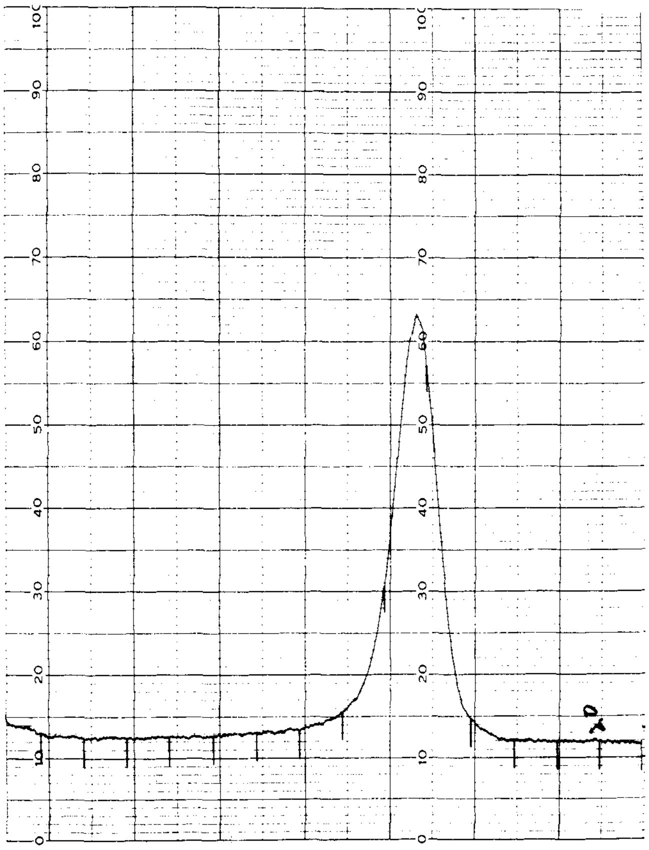

Figure 1. GPC chromatogram of poly(styrene–butadiene–styrene).

diene block was polymerized in the same manner as that described in the gelation test. In one run the presolubilization of the initiator dispersion was used as described. In a second run the presolubilization step was omitted and the entire amount of butadiene monomer was introduced prior to the addition of the initiator dispersion. After the completion of butadiene polymerization the reaction mixture was cooled to approximately 35 °C. Purified styrene monomers of approximately one-third of the weight of the butadiene used and 2 mL of freshly distilled tetrahydrofuran were added. Polymerization of styrene took another hour. After glacial acetic acid was used to terminate the anions, the copolymer was recovered by precipitation with methanol and drying under vacuum. The GPC chromatograms of both runs were nearly alike. Figure 1 shows the chromatogram for the second run in which the initiator dispersion was used directly. The calculated M_w/M_n ratio for this run was 1.4, broader than the M_w/M_n ratio of 1.2 for the first run in which the initiator dispersion was solubilized before use. The compression molded specimens of both samples gave nearly alike tensile properties: tensile rupture strength of over 3200 psi and total elongation of over 950%. These properties are comparable to those reported elsewhere[13,14] for poly(styrene–butadiene–styrene).

The above results convinced us that the addition products of *sec*-butyllithium and double 1,1-DPE compounds are useful dilithium initiators.

References and Notes

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Radiation Degradation of Poly(methacrylates)

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Methacrylate polymers have been the subject of many investigations concerning polymer radiation degradation induced by exposure to ionizing radiation.[2a] Poly(methyl methacrylate), PMMA, has been the most extensively studied and is found to predominately degrade with essentially no concurrent cross-linking.[2b,3] Graham has looked at the radiation behavior of several other poly(alkyl methacrylates) and reported that significant yields of concurrent cross-linking occur when the alkyl group is long and not branched.[4] Kircher et al.[5] find that the four isomeric butyl methacrylate polymers also predominately degrade; ester group loss and chain scission processes, however, were determined to be dependent upon ester group structure.

PMMA is an important polymer to the electronics industry because it functions as a high-resolution e beam[6] or x-ray[7] resist and is capable of integrated circuit element pattern delineation production processing. Since it has been shown that radiation *G* values correlate with e-beam sensitivity,[8] we report the radiation *G* values for several other methacrylate polymers of interest on the basis of their chemical structures.

Poly(*tert*-butyl methacrylate), PTBMA, and poly(isobutyl methacrylate), PIBMA, isomeric methacrylate polymers, are reinvestigated because they were previously reported to be more sensitive toward radiation degradation than PMMA[5] on the basis of chemical analysis and molecular weight determinations. Unfortunately, only one absorbed dose, namely 30 Mrad, was employed for these determinations and the polymers had fairly low unirradiated molecular weights; for this reason, no radiation *G* values were reported from the molecular weight data. We have irradiated PTBMA and PIBMA to a series of lower doses, where the determined $\overline{M}_n^{-1}$ values are linear with dose, to obtain quantitative *G* values for comparison to the *G* value of PMMA. In addition, we report results for poly(benzyl methacrylate), PBZMA, poly(cyclohexyl methacrylate), PCHMA, and copolymers of *n*-hexyl methacrylate (NHMA) and methyl methacrylate. The latter systems were chosen over PNHMA to insure that all test polymers had glass transition temperatures above room temperature.

Poly(*tert*-butyl methacrylate) (PTBMA) and poly(benzyl methacrylate) (PBZMA) were obtained from Aldrich Chemical Co., and Polysciences, Inc., respectively. The polymers were purified by twice precipitating them from solvents. Both the homopolymer poly(cyclohexyl methacrylate) (PCHMA) and the copolymers of *n*-hexyl methacrylate and methyl

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