

The Preparation of Some Block Copolymers

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Synopsis

The reactivity of the double bonds in *p*-divinylbenzene toward anionic reagents is much greater than is the residual double bond in the divinylbenzene unit incorporated in a polymer chain. Thus it is possible to add to a "living" polymer a few divinylbenzene units before appreciable crosslinking occurs. Each of these units will have a vinyl group conjugated with a phenyl ring and will be comparable in reactivity to styrene. If the reaction is stopped at this point by the addition of methanol, the molecular weight of the product is essentially that of the original living polymer. These polymers may then be copolymerized through these active double bonds with any monomer with which styrene may be copolymerized, to form block or graft-like copolymers. The copolymerizations may be effected by any of the methods applicable to styrene, i.e., free radical, cationic, or anionic. Such copolymerizations have been attempted with methyl methacrylate, butyl acrylate, vinyl chloride, vinylidene chloride, vinyl acetate, butadiene, isobutene, and propene, usually successfully.

INTRODUCTION

The preparation of block copolymers by anionic methods is a well-known technique^{1,2} as is the modifications of reacting a living polymer with suitable reagents to create a reactive endgroup capable of coupling with another polymer system. Polymers have also been prepared with unsaturated endgroups by reacting living polymers with allyl halides,³ and these double bonds may then be used as centers for further polymerization. Described here is the preparation of polymers terminated with vinyl groups activated by phenyl groups by reacting living polymers under suitable conditions with *p*-divinylbenzene (*p*-DVB), and this styrene-like endgroup is then particularly susceptible to further polymerization with other monomers to give block or graft-like copolymers.

Earlier, in a study of the anionic polymerization of aromatic divinyl monomers,⁴ soluble polymers were obtained only when one of the vinyl groups was conjugated with the phenyl ring, leaving the other vinyl group unreactive to anionic polymerization. But by taking advantage of the reactivity difference of the first polymerized and the remaining vinyl group, short linear chains of *p*-DVB may be added as a block on the end of a suitable living anionic polymer chain if the reaction is terminated before the second group has time to react. If the reaction is not terminated at this point, star-shaped polymers are formed.⁵

Suitable living polymers include those of styrene, α -methylstyrene, butadiene, and isoprene, or any monomer giving an anion of sufficient reactivity to react with *p*-DVB, polymerized with an anionic initiator, preferably in a hydrocarbon solvent to give better control over the rate processes. The *p*-DVB may be added, either in hydrocarbon or ether (e.g., THF) solution, when all the first monomer has reacted. At room temperature in benzene solution, the rate of reaction of the first vinyl group is about ten times that of the second group to react,⁶ so it is possible to add several *p*-DVB molecules before appreciable crosslinking occurs. If the reaction is terminated at this point by the addition of a killing agent such as methanol, the isolated polymer has the same molecular weight as the original but can be shown to contain a few vinyl groups conjugated to phenyl, as judged from an ultraviolet absorption peak at 296 $m\mu$, this is comparable to the absorption of styrene at 292 $m\mu$.

These polymers may then be reacted with other monomers and may be copolymerized by any of the methods whereby styrene, treating styrene as the model, may be copolymerized, i.e., by radical, cationic, and anionic initiators, provided the reactivity ratios are suitable. The second monomer starts a chain and incorporates the first polymer end groups by the normal copolymerization process leaving the first chain as a side group, or branch. In theory several chains could be incorporated by this process, but in practice often only one is.

EXPERIMENTAL

The solvents and monomers used for the first anionic polymerization were purified as described elsewhere.⁷ The monomers for the free-radical and cationic polymerizations were dried with calcium hydride and distilled on a vacuum line.

The *p*-DVB was isolated from the Dow commercial DVB mixture by forming the cuprous chloride complex by the method of Rubinstein and Snyder.⁸ The cuprous chloride treatment was repeated to give a product of better than 95% purity, which was crystallized from methanol to 99.8%. This product was vacuum distilled to free it from methanol and immediately before use, dried over calcium hydride for 1 hr.

The first block polymers were prepared from 10% solutions of the monomers, styrene or isoprene, at room temperature using *sec*-butyllithium (Foote Mineral Co.) as the initiator. The *p*-DVB, dissolved in THF, three times the molar quantity of butyllithium, was added after 16 hr, and the reaction was terminated 2 min later with methanol. α -Methylstyrene was similarly polymerized at 0°C for 48 hr in 20% solution; the calculated molecular weight was based on a 50% yield because of the monomer-polymer equilibrium.⁹ All manipulations were carried out in sealed glass apparatus fitted with breakseals to give 50 g of product. Usually the copolymerization with the second monomer was carried out with 5 g of the first block.

The radical second polymerizations were normally in benzene at 60°C, with azobisisobutyronitrile as the initiator, except for some emulsion polymerizations where potassium persulfate was used in a typical recipe.

Most of the cationic polymerizations with isobutene were done at -80°C in toluene solution, using BF₃ as initiator. The Ziegler copolymerization with propene used a 4:1 ratio of aluminum triethyl to titanium tetrachloride at room temperature, with an initial pressure of 1 atm of propene.

Separation of homopolymers from block copolymers was attempted by solvent extraction in a Soxhlet. Frequently the extracting solvent was milky, and separations were seldom clean.

All molecular weights were measured on a Mechrolab high-speed membrane osmometer, in toluene solution.

RESULTS

The polymers isolated after the addition of the *p*-DVB were found to have nearly the same molecular weight as that of a sample of the polymer isolated before its addition. Some typical polymers are shown in Table I.

TABLE I
Molecular Weights of Base Polymers

Monomer	\bar{M}_n of polymer	\bar{M}_n of polymer + DVB
Styrene	42,000	42,000
Styrene	21,100	21,500
Styrene	28,000	33,000
α -Methylstyrene	35,500	38,000
α -Methylstyrene	29,500	30,500

Their ultraviolet spectra showed that the polymers had one or two styrene-like double bonds per chain, assuming the same extinction coefficient as for styrene. These polymers are referred to as base polymers.

Copolymers with Methyl Methacrylate

The best conditions for the copolymerization would be expected when the reactivity ratios are nearly equal and close to unity, as happens for methyl methacrylate and styrene in radical polymerizations. Table II shows the result of so polymerizing three different base polymers and solvent extracting the products. Cyclohexane was used to extract the residual base polymer, and acetonitrile, to remove any homo-PMMA, although, as usually happened, some copolymer was removed at the same time. In all three cases, most of the product was incorporated in a copolymer, although in the case of poly- α -methylstyrene (PAMS), where the reaction was taken almost to completion, more homopolymer was present. The rather large amount dissolved out by acetonitrile from the product of the reaction with

TABLE II
Copolymerization with Methyl Methacrylate

Base polymer	Ratio of base polymer to MMA	Yield ^a	Sol in MeCN ^b	Sol in cyclohexane	MW of residual polymer
Polystyrene (22,000)	1:2	2.4	0	0	70,000
PAMS (35,000)	1:2	2.8	0.73	0.22	60,000
Polyisoprene	1:4	2.5	0.75	—	—

^a The yield is based on unity as the starting weight of base polymer.

^b MeCN = Acetonitrile.

the polyisoprene base polymer contained appreciable amounts of polyisoprene, presumably in the form of copolymer.

As would occur in a normal copolymerization, only partial conversion of the second monomer should result in only partial incorporation of the first block, and this is shown in Table III. In the last two experiments, 30–35% conversion of the MMA resulted in 40–50% consumption of the initial PAMS block. In the first experiment, evidently all the PMMA was incorporated into the copolymer but, owing to a short block length, was soluble in cyclohexane and could not be separated from the remaining base polymer. In the last two experiments, it is evident from the molecular weight of the block copolymer and its composition that three or four PAMS blocks are incorporated into each molecule.

TABLE III
Copolymer Formed from PAMS (30,500) and MMA

Ratio of base polymer to MMA	Yield ^a	Sol in cyclohexane	Sol in MeCN ^b	PMMA in insol. polymer, %	MW of residual polymer
1:0.5	1.20	1.20	—	—	—
1:1	1.35	0.6	0	48	186,000
1:1.5	1.50	0.5	0.1	45	238,000

^a The yield is based on unity as the starting weight of base polymer.

^b MeCN = Acetonitrile.

In a blank experiment, MMA was polymerized in the presence of PAMS without the *p*-DVB ending, and the product was separated nearly quantitatively into the two homopolymers. This shows that the addition of the PMMA is not a simple grafting reaction, but occurs through the terminal vinyl endgroups.

Copolymers with Butyl Acrylate

The polymerizations were under the same conditions as for MMA and were taken to about 50% conversion. In the extraction, first free PBA was removed with hexane, and then the copolymer was extracted with ace-

TABLE IV
Copolymer Formed from PAMS (18,500) and Butyl Acrylate

Ratio of base polymer to BA	Yield	Sol in hexane	Sol in acetone	Residue	MW of acetone sol
1:0.67	1.3	0	1.1	0.2	21,700
1:1	1.67	0.17	1.5	0	30,500
1:2	2.2	0.18	1.84	0.2	41,500

tone to leave the starting PAMS as residue. The results are in Table IV, showing that most of the butyl acrylate is in the copolymer. Also most of the PAMS has reacted, presumably because of the more favorable reactivity ratio for the incorporation of styrene-like double bond. The molecular weight is much lower than for the MMA case, and probably a transfer reaction occurs.

Other Radical Copolymerizations

The reactivity ratios for the reaction with butadiene are favorable, and emulsion copolymerization of polystyrene base polymers with mixed butadiene and styrene monomers by a typical GSR rubber recipe was attempted. Unfortunately no satisfactory method of separating the polymers was found, but no nonrubbery components were found, suggesting that the polystyrene was incorporated into the copolymer as expected.

Copolymerizations with vinyl chloride and vinylidene chloride were attempted. Both monomers could be expected to add freely to the styrene-like endgroup. Evidently, both monomers did add on to the base polymer, in this case PAMS, as in several polymerizations taken to yield 20–30% all the product from the vinyl chloride reaction was soluble in cyclohexane, and all the product from the vinylidene chloride reaction was extracted by chloroform although the homopolymers of these monomers are not soluble in these solvents. Further separation of the vinyl chloride copolymer was not successful, but the product only appeared to incorporate one chain of the base polymer per molecule. The portion of the product from the vinylidene chloride reaction not soluble in cyclohexane only gave cloudy solutions in all solvents tried, and no molecular weights could be determined. Vinyl chloride will graft onto PAMS even when the polymer contains no double bonds, but in the reactions with the PAMS base polymer with double bonds, the double bonds did disappear, as shown by the disappearance of the ultraviolet absorption at 296 m μ .

Copolymerizations with vinyl acetate resulted in large yields of block copolymers with both PAMS and polystyrene base polymers, despite the unfavorable reactivity ratios. Analysis of the molecular weights and compositions of the copolymers suggested that the products were formed from PAMS by breaking the polymer chain and adding vinyl acetate to the ends. Some type of grafting probably occurs with polystyrene, despite suggestions in the literature to the contrary.^{10,11}

Another monomer with an unfavorable reactivity ratio was chloroprene. As expected, little or no copolymer formed with PAMS base polymer, but for polystyrene most of the product was soluble in methyl ethyl ketone suggesting that grafting had occurred, as opposed to reaction at the terminal double bond.

Cationic Copolymerization

In principle, it should be possible to incorporate the base polymers into block copolymers by a cationic mechanism as well. The reactivity ratios for isobutene and the model styrene are favorable, and Table V lists some of the results. The separation of the homopolyisobutene was by extraction with pentane; for homopolystyrene, methyl ethyl ketone was used. The

TABLE V
Copolymer Formed from Base Polymer and Isobutene

MW of base polymer	Ratio of base polymer to isobutene	Yield	Sol in pentane	Sol in MEK	MW of residual polymer
Polystyrene ^a					
42,000	1:1	2.0	0.12	0.6	
22,000	1:1.6	2.6	1.55 ^b	0.5	
22,000	1:1.6	1.5	0	0.84	141,000 ^b
21,500	1:3	3.7	0.25	0.1	57,400
21,500	1:1.4	2.3	0.12	0.6	42,000
PAMS					
38,000	1:2	2.8	0.65	0.19	73,000

^a The first two had TiCl₄ as catalyst, the rest, BF₃.

^b Contained 39% polystyrene.

extracting solutions were often cloudy and contained appreciable amounts of the copolymer. It is evident that most of the product was copolymer, although usually the molecular weight is only consistent with a 2-block copolymer. The exception was one reaction which did not go to virtual completion and contained 2 or 3 blocks of polystyrene per molecule. Normally polyisobutene prepared under these conditions would have a molecular weight of over 100,000, so transfer again occurs, and in fact a polyisobutene prepared in the presence of normal polystyrene also had a low molecular weight.

Copolymerization with Ziegler Catalyst

All the above reactions were with homogeneous catalyst systems and starting conditions, although in several cases the product precipitated either as a gel or powder, or the solution became cloudy. To see if copolymerization could be effected with a heterogeneous catalyst, a base polymer of polystyrene was reacted with propene and a typical Ziegler

catalyst. The final product contained 50% polystyrene and was extracted with methylene chloride. The extract constituted 65% of the total and contained all of the polystyrene. After further extraction with methyl ethyl ketone, there remained of this extract a rubbery residue (28% of the original material) containing 37% styrene, which must have contained the block copolymer. This, however, probably contained some low molecular weight homo-polypropene as well as the block copolymer, as its molecular weight was comparable to that of the base polymer. Thus the yield of this block copolymer is lower than that obtained with a homogeneous catalyst system under the conditions used here.

CONCLUSIONS

It is evident that where monomers are chosen whose reactivity ratios with the styrene model are not too far from unity, block copolymers are freely formed with these base polymers containing the styrene-like end-groups, at least with homogeneous catalyst systems. When the conversions are not too high, almost complete incorporation of the second monomer is achieved, leaving some unchanged base polymers.

The molecular weights of the products are usually lower than would be expected from the homopolymerization of the second monomer under similar conditions, or even from normal copolymerization with styrene. No explanation has been found for this, but the molecular weights often appear higher at lower conversions. In the case of addition of monomers which in polymerization give a highly active polymer radical, such as vinyl acetate or vinyl chloride, the copolymerization reaction is in competition with a grafting reaction, and in these cases there is less advantage to this method of forming block copolymers. For other monomers whose polymer radical is better stabilized, the method is very effective.

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