The Reaction of Vinyl Monomers with "Trapped Free Radicals"

Raymond B. Seymour[a]; G. Allan Stahl[b]

[a] Department of Polymer Science, University of Southern Mississippi, Hattiesburg, MS [b] B. F. Goodrich R & D Center, Brecksville, OH

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Raymond B. Seymour
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39401

G. Allan Stahl
B. F. Goodrich R & D Center
9921 Brecksville Road
Brecksville, OH 44141

ABSTRACT

Previous attempts to prepare copolymers by the reaction of vinyl monomers, such as styrene, with "trapped free radicals" such as acrylonitrile macroradicles has been unsuccessful because of the large differences in solubility parameters between the liquid and the solid. However, acrylonitrile will react with styrene macroradicals in the absence of oxygen, and yield block copolymers. Block copolymers may be produced from other vinyl monomers and other macroradicals when the difference in the solubility parameter of the monomer and macroradicals is less than 3.2H.

INTRODUCTION

It has been observed, for many years, that some polymers, such as polyacrylonitrile (PAN), polyvinyl chloride, (PVC), polyvinylidene chloride (PVDC), and polytrifluorochloroethylene are insoluble in their monomers and that these polymers precipitate when the monomers are polymerized by free radical-initiated polymerization, in the absence of solvents.

While the macroradicals continued to grow, as evidenced by an increase in the degree of polymerization (DP), other vinyl monomers, such as styrene, did not add to these macroradicals. This investigation was undertaken in order to ascertain proper conditions for such addition reactions and thus to produce novel copolymers by the reaction of vinyl monomers and "trapped free radicals".

EXPERIMENTAL

Macroradicals were obtained by heating a 10 percent solution of freshly distilled monomers in a selected solvent at 50°C in the presence of 20 percent azobisisobutyronitrile (AIBN) (based on monomer) and in the absence of oxygen. Oxygen was eliminated from the system by bubbling zero grade-nitrogen through the solution for 30 min. at room temperature.

The mixture was heated for seven days at 50°C to assure the absence of primary free radicals before adding the new monomer to the slurry in a glove bag type dry box in the absence of oxygen.

The products were obtained by filtering in Gooch crucibles and washing the residual solids with new solvent. The washed solids were dried at 100°C for 24 hours and cooled in a vacuum desiccator for 12 hours.

The solvent-free samples were dissolved in a good solvent and the homopolymers and block copolymers were precipitated separately by the addition of selected nonsolvent, filtered and dried. The solvent-free polymeric products were characterized by pyrolysis gas chromatography, turbidimetric titration, infra red spectroscopy, and differential thermal analysis.

DISCUSSION

It was observed previously that the rate of polymerization of vinyl chloride[1] and acrylonitrile was accelerated in the presence of polymer which had precipitated because it was insoluble in the monomer[2]. This effect was not noted when dead PAN was present and the acceleration was attributed to the presence of "trapped free radicals"[3].

The latter were characterized by electron spin resonance spectroscopy (ESR) and by coupling with diphenyl picryl hydrazyl (DDPH)[4]. It was also shown that the "trapped free radicals" or macroradicals were terminated by the presence of traces of oxygen and were not produced when acrylonitrile was polymerized in a good solvent, such as dimethylformamide (DMF).

Acceleration of polymerization was also observed when styrene was polymerized in a poor solvent, such as methanol[5] or 1-hexane[6]. Other macroradicals have also been obtained by the polymerization of acrylonitrile[7], methyl acrylate[8] and equal mixtures of styrene and maleic anhydride[9] in poor solvents.

The criterion for a poor solvent was that the difference in solubility parameter between the polymer and solvent be at least 1.8 Hildebrand units (H)[10, 11, 12]. The rate of polymerization was fastest when the difference was 1.8H and decreased as this difference in solubility parameters increased[13].

Acrylonitrile and vinyl chloride will diffuse into macroradicals of these monomers and produce higher molecular weight homopolymers. However, other monomers will not diffuse into these macroradicals unless the difference in the solubility parameters of the monomer and macroradical or polymer is less than 3.2H[14].

This explains why it is not possible to produce a block copolymer by adding styrene monomer (9.2H) to acrylonitrile (13H). Yet, some block copolymer is produced when DMF is added dropwise to a slurry of acrylonitrile macroradicals in benzene and styrene. Of course, only dead polymer is obtained when acrylonitrile is polymerized in DMF.

Since styrene and acrylonitrile form a charge transfer complex which has a solubility parameter of 10H, a block copolymer ie, poly (acrylonitrile-b-styrene-co-acrylonitrile) is produced when an equimolar mixture of styrene and acrylonitrile is added to a slurry of acrylonitrile macroradicals in benzene. Likewise, while neither styrene nor maleic anhydride will form a block copolymer with acrylonitrile macroradicals, a block i.e., poly (acrylonitrile-b-styrene-co-maleic anhydride) is produced when equimolor quantities of styrene and maleic anhydride (11.0H) are added to a slurry of acrylonitrile macroradicals. When an excess of styrene monomer is present, the product is poly (acrylonitrile-b-styrene-co-maleic anhydride-b-styrene)[15].

While styrene (9.2H) will not diffuse into macroradicals of acrylonitrile (13.H), acrylonitrile (10.8H) will diffuse into styrene macroradicals (9.1H) dispersed in 1-propanol. The resulting block copolymer, of course, is identical to that which cannot be readily prepared by the addition of styrene to acrylonitrile macroradicals

Styrene macroradicals may be produced in a poor solvent, such as 1-propanol (11.9H) and in a nonpolar solvents, such as 1-hexane (7.3H)[16]. Block copolymers are readily produced when vinyl monomers are added to these macroradicals.

Block copolymers have also been produced by the addition of vinyl monomers to macroradicals of methyl methacrylate[17], vinyl acetate[18], and styrene-maleic anhydride[19]. The length of the

styrene block of the latter is limited to about 30 percent of that of the macroradical when the block is prepared in benzene. However, larger blocks may be prepared in solvents which are both nonsolvents for styrene-maleic anhydride copolymer and polystyrene.

It is difficult to prepare stable macroradicals of monomers, such as methyl acrylate, with low Tg values. This restriction, based on mobility, also applies to blocks of monomers with low Tg values. Likewise, blocks cannot be prepared at temperatures above the theta temperature. Thus, while good yields of poly (methyl methacrylate-b-acrylonitrile) are obtained by heating a slurry of methyl methacrylate macroradicals and acrylonitrile in 1-propanol at 70°, the yields decrease as the temperature is increased. The theta temperature of this system is 82°.

Macroradicals are also stable in viscous good solvents and block copolymers may be produced by the addition of vinyl monomers to viscous solutions of macroradicals. The yield of block copolymers in poor solvents is also increased when the polymerization takes place in viscous poor solvents[20].

The yield and molecular weight of styrene macroradicals was increased when these macroradicals were produced in silicone oils of increasing viscosities[21]. Likewise, the degree of dispersity decreased as styrene continued to add to these styrene macroradicals. The lowest value for the degree of dispersity was noted after long time polymerization in the highest viscosity silicone oils.

CONCLUSION

Block copolymers are readily produced by the reaction of vinyl monomers with stable macroradicals in poor solvents. The efficiency and rate of formation of block copolymers is increased in viscous systems.

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