

Synthesis of Reactive Oxazolyl Styrene–Acrylonitrile Copolymers

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SYNOPSIS

A series of oxazoline-modified styrene–acrylonitrile (SAN) copolymers was prepared through the reaction of amino alcohols onto preformed SAN copolymers. Consequently, a variety of reactive copolymers were synthesized. The major focus of this study was to examine the influence of reaction conditions, i.e., the nature of the catalyst and amino alcohol structure, on reactivity. The ability to incorporate oxazoline groups onto preformed polymers is dependent on whether homogeneous reaction conditions are met. For example, the use of nonreactive solubilizing agents, i.e., cosolvent, is effective. However, optimum conditions are obtained when the catalyst is completely soluble in the reaction mixture containing the amino alcohol and SAN copolymer. With these restrictions, zinc stearate is quite effective. Our results show that controlled and reproducible levels of oxazoline can be incorporated (typically at a rate of 2 mol %/h) up to high levels. These results are general and therefore are applicable to a wide variety of nitrile-containing polymers. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The modification of the structure of polymeric materials has recently emerged as an extremely active field in polymer science.^{1–5} An increasing variety of chemical reactions have been employed to produce polymers with novel and desirable physical and chemical properties. These reactions can be utilized to introduce functional, e.g., ion-containing polymers, and reactive groups, e.g., maleated polypropylene. This recent upsurge in interest in these types of polymers has been sparked in large part by their use as compatibilizers in blends.

A majority of binary component blends are immiscible and therefore possess poor interfacial characteristics and poor mechanical properties. Blending is substantially enhanced with the addition of polymers of complementary functional groups such as in rubber-toughened blends containing groups that interact via coordination-type associations.⁶ In a similar manner, reactive processing

techniques are used. For example, nylon 6 is rubber-toughened through the reaction with ethylene–propylene–diene terpolymer (EPDM) containing low amounts of maleic anhydride (EPDM–MA).⁷ Since nylon 6 contains one terminal amine group, its reaction with EPDM–MA produces a product that is a graft copolymer essentially free of crosslinking. These polymeric compatibilizers, whether formed through associations of complementary groups or chemical bonding between reactive functionalities, lower surface tension, promote interfacial adhesion, and substantially improve the size and distribution of the dispersed phase. Improved mechanical properties result. However, it is quite apparent that a large number of commercially available polymers cannot be easily and effectively utilized under reactive processing conditions.

This report details the incorporation of relatively low levels of oxazoline functionality onto styrene–acrylonitrile (SAN) copolymers. The synthetic procedure incorporates in a facile manner these reactive groups onto preformed SAN copolymers. As a result of this modification, a wide variety of reactive SAN copolymers can be produced spanning a range of acrylonitrile and oxazoline content. It is noteworthy

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that unfunctionalized SAN copolymers are miscible with a number of polymers including poly(methyl methacrylate)⁸ and poly(ϵ -caprolactone),^{9,10} but its major use is in rubber-toughened blends.¹¹ The addition of reactive groups in SAN copolymers should broaden the usefulness of these polymers.

It is noteworthy that the chemical modification of SAN is a rather new topic. Kopic et al.¹² demonstrated the alkaline hydrolysis of SAN copolymers: The reaction rates decreased in the order dioxane > ethanol > water. Also, compared to the random copolymer, the alternating SAN copolymer showed the highest resistance toward hydrolysis. Roizard et al.¹³ were able to conduct the *para*-acylation of the styrene moiety in SAN copolymers. In spite of the use of varied acylating conditions, they found the upper limit of the conversion was 50% and attributed this phenomenon to microenvironment effects.

The synthesis and reactivity of low molecular weight oxazolines were described by Witte and Seeliger,¹⁴ Frump,¹⁵ and Wiley and Bennett.¹⁶ More recently, the syntheses and polymerization of cyclic 1,3-oxazoline compounds was reviewed by Saegusa et al.¹⁷ The transformation of nitrile to oxazoline groups was developed by Seeliger et al.,¹⁷ and in this report, this method has been extended to prepare a wide variety of polymers containing the 2-oxazoline functionality.

EXPERIMENTAL

The SAN copolymer used in this study was obtained from Monsanto Co. (Lustran[®]) and were used as received. The SAN copolymer contained 30 mol % acrylonitrile determined by elemental analysis: 4.73 wt % nitrogen and ¹H-NMR analysis. Zn(OAc)₂·2H₂O, Cd(OAc)₂·2H₂O, zinc stearate, dibutyltin dilaurate, *n*-butanol, 2-aminoethanol (2AE), 2-methyl-2-amino-1-propanol (2MP), 1,2-dichlorobenzene (DCB), chloroform, and methanol were used as received (Aldrich Chemicals).

¹H-NMR spectra were obtained from a Varian XL-300 instrument. Infrared spectra were taken on a Perkin-Elmer 238 infrared spectrometer.

The preparation of oxazoline-modified SAN from SAN copolymer was conducted under a variety of conditions. Modification in the reaction temperature, time, concentration, catalyst, and amine structure were of interest. Further detailed studies will be the subject of a future publication. A typical synthesis procedure is described as follows:

Zinc stearate, 3.0 g (4.75 mmol), is dissolved into a 200 mL DCB solution containing 20 g SAN copolymer (38.2 mmol nitrile) at 140°C. Subsequently, 9.6 g (157 mmol) 2AE is introduced into the mixture. The reaction temperature was kept constant at 140°C for 4.5 h. Aliquots were obtained and the polymer isolated in order to determine conversion (¹H-NMR) as a function of time. The remaining reaction mixture was cooled to room temperature and diluted with 200 mL chloroform. The polymer was precipitated from methanol by dripping the chloroform solution along the wall of a 2 L flask with vigorous agitation. A volume ratio of 10 : 1 (methanol-to-polymer solution) was typically used. The precipitated polymer was dissolved in 300 mL chloroform and again precipitated in methanol under the previously described conditions. Yield was 94% based on the recovered copolymer. Deuterated methylene chloride was used for the ¹H-NMR analysis.

RESULTS AND DISCUSSION

As noted previously, Witte and Seelinger¹⁴ developed a method to synthesize 2-oxazolines containing a wide variety of aliphatic and aromatic derivatives. These products were nonpolymeric and were prepared by the reaction of nitriles with amino alcohols and catalytic concentrations of specific metal salts. The reaction conditions are mild. Although the reaction mechanism remains obscure, we found in our reaction systems that chelation of the nitrile group to the metal ion is a necessary condition for a reaction to occur. Through this step, the nitrile group becomes active and is able to react with 2-amino alcohols.

Our synthesis procedure involved the following catalysts: dibutyltin dilaurate, cadmium and zinc acetate, and zinc stearate. Dibutyltin dilaurate is extensively used as a catalyst for preparing, e.g., polyurethane and poly(ϵ -caprolactone). Even though this catalyst is completely soluble in the reaction mixture, SAN copolymers were not functionalized.

The occurrence of the oxazoline modification was determined through ¹H-NMR analysis. The ethylene unit within oxazoline can be detected at δ 3.0–4.2. For most of the monomeric oxazolines and pendent oxazoline groups far from the polymer backbone, the chemical shifts were observed at δ 3.5–4.5.¹⁸ However, for a commercially available polymer, reactive polystyrene (Dow Chemical Co.) composed of styrene and isopropenyl-2-oxazoline (1% by weight), similar chemical shifts to the modified SAN copol-

Table I Reaction Conditions and SAN Copolymer Conversion Using Cadmium Acetate as Catalyst

Amino Alcohol Structure ^a	Reaction Temperature (°C)	Reaction Time (h)	Reactant Concentration ^b (mol)	Oxazoline Content ^c (mol %)
2MP	135	5	0.051 : 0.059 : 0.0046 : 115	6
	170	9	0.034 : 0.078 : 0.00619 : 50	30
2AE	135	5	0.034 : 0.078 : 0.000619 : 100	2.2
	170	5	0.034 : 0.078 : 0.0619 : 50	13.5

^a 2MP: 2-methyl-2-amino-1-propanol. 2AE: 2-amino ethanol.

^b Reactant concentrations are in the following order: acrylonitrile : amino alcohol : catalyst:solvent (1,2-dichlorobenzene, mL).

^c Nitrile-to-oxazoline conversion was determined from ¹H-NMR analysis by comparing the integration of δ 0.8–2.9 to δ 3.1–4.3.

ymers are noted. The slight shift in δ is probably due to the ring current of the neighboring phenyl group. The IR spectra of the modified SAN copolymers showed an absorption band at 1650 cm⁻¹, a characteristic feature of the oxazoline structure. Also, the vanishing of the nitrile adsorption band at 2200 cm⁻¹ was noticed.

To explore the effectiveness of homogeneous and heterogeneous reaction conditions, cadmium acetate was selected. The solubility characteristics of this salt were determined and the results show that a homogeneous mixture was formed with 2MP, while heterogeneous conditions occurred with 2AE. The results of these reactions under a variety of conditions are presented in Table I.

An examination of the results in Table I shows that cadmium acetate is a relatively good catalyst for the oxazoline modification of SAN copolymers. However, it is found that cadmium acetate is more effective with 2MP than with 2AE. This phenomenon has been further explored and we note that homogeneous conditions are an important factor in obtaining a near-quantitative product modification. Undoubtedly, homogeneous conditions ensure an intimate contact of the reactants with the catalyst.

These results are further clarified with the use (or absence) of a solubilization agent for the catalyst. In our studies, the catalyst was zinc acetate and the solubilization agent is *n*-butyl alcohol. The detailed data are presented in Table II. These preliminary findings confirm that addition of a solubilization agent markedly enhances the reactivity of the catalyst toward 2AE. Without *n*-butyl alcohol, no reaction was observed, while substantial functionalization took place with a moderate amount of the solubilization agent. In the former reaction scheme, a two-phase system, i.e., solid and liquid, was clearly visible. Although during the reaction a minute amount of catalyst is likely to be soluble, there is apparently an insufficient quantity dissolved to have a quantitative influence on reactivity. It is noteworthy that no reaction was observed in 2MP with *n*-butyl alcohol, even though it was a single-phase solution system. The reason for this behavior is presently being examined.

Using zinc acetate in conjunction with a solubilization additive seems to be a promising approach for forming oxazoline SAN copolymers. However, the dissolution rate of zinc acetate needs to be enhanced. Presently, the optimum conditions are to

Table II Reaction Conditions and SAN Copolymer Conversion Using Zinc Acetate as Catalyst

Amino Alcohol Structure ^a	Reaction Temperature (°C)	Reaction Time (h)	Reactant Concentration ^b (mol)	Oxazoline Content ^c (mol %)
2AP	135	7.0	0.036 : 0.589 : 0.00684 : 50 : 0.0	0.0
2AP	135	7.0	0.036 : 0.0589 : 0.00684 : 50 : 15	9.1
2MP	135	7.0	0.034 : 0.0589 : 0.0684 : 50 : 10	0.0

^a 2AP: 2-amino ethanol. 2MP: 2-methyl-2-amino-1-propanol.

^b Reactants are in the following order: acrylonitrile : amino alcohol : catalyst : solvent (1,2-dichlorobenzene, mL) : *n*-butylalcohol (mL).

^c Determined by ¹H-NMR (see Table I for details).

dissolve the SAN copolymer into DCB at 65°C, elevate the temperature to 135°C, and then introduce *n*-butyl alcohol, 2AE, and, lastly, zinc acetate.

The particle size of the zinc acetate is a factor in reactivity. Again, this is apparently related to the kinetics of dissolution. If a crystal form of zinc acetate is used (average particle size as determined by light microscopy is approximately 100 microns), little reaction takes place. The reaction conditions are identical to those detailed in Table II, except the reaction time was 0.5 h. Reducing the particle size to approximately 10 microns substantially improves the catalyst's performance. Typical oxazoline contents are between 3 and 4 mol %.

To reproducibly form reactive SAN copolymers spanning a wide range of functionalization, a completely soluble catalyst is obviously required. The use of zinc stearate meets this requirement. This compound is completely soluble in the mixture of DCB and 2AE at reaction temperature. Figure 1 shows the effect of reaction time on oxazoline functionalization. The reaction conditions are identical again to the specifications in Table II. A linear relationship is found with a slope of approximately 2 mol %/h. Under these conditions, the oxazoline level can be precisely controlled up to relatively high levels. We have not attempted to maximize conversion since these polymers are useful in reactive processing for blend compatibilization. If the reactive functionality is too high, blend compatibilization could be retarded due to extensive gel formation. The utilization of oxazoline-modified SAN copolymers in blend compatibilization has been extensively examined and will be the subject of future publications.

CONCLUSIONS

A variety of synthetic procedures were devised in order to incorporate oxazoline functionality into nitrile-containing copolymers, specifically, styrene-acrylonitrile copolymers. This reactive group is of interest because of its facile reactivity with a relatively wide range of complementary reactive groups. The results show that oxazoline addition can be accomplished under relatively mild conditions using amino alcohols and soluble metal-containing catalysts. Although changing the nature of the metal ion, and its effect on reactivity, still requires more extensive experimentation, it is apparent that zinc stearate is clearly effective in controlling the functionalization level. This is due primarily to its solubility in the reaction medium. Alternatively, slightly soluble catalysts form essentially two-phase

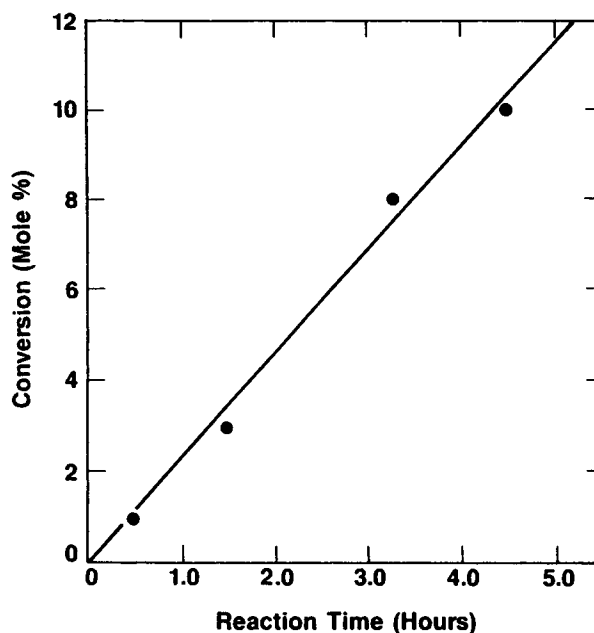


Figure 1 Conversion of nitrile to oxazoline groups in a SAN copolymer (30 mol % acrylonitrile content) as a function of reaction time using a soluble catalyst, i.e., zinc stearate. Reaction conditions are given in Table II.

systems, resulting in poorly controlled reaction conditions.

Furthermore, the nature of the amino alcohol can influence reactivity, especially if a two-phase system develops. As with the catalyst structure, it is not known whether reactivity is enhanced with structural modifications in the amino alcohol. In addition, it is not apparent which oxazoline type is most suitable in forming a compatibilizer with a specific polymer family. A number of these studies are presently underway.

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Received November 28, 1994

Accepted December 18, 1994