

Chemical Transformation of Nitrile to Reactive Oxazoline Functionality on a Preformed Polymer

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SYNOPSIS

The chemical transformation of nitrile to oxazoline functionality via a soluble zinc salt-catalyzed reaction was conducted on a series of nitrile-containing copolymers, i.e., styrene-acrylonitrile (SAN) and nitrile rubbers. The results show that triad tacticity of the acrylonitrile groups is important in understanding the relative reactivity of SAN copolymers. Furthermore, the dielectric properties of the comonomer is also a prime factor in understanding the different degrees of reactivity of SAN, nitrile rubbers, and its hydrogenated analog forms. Enhanced reaction rates are noted with higher dielectric constants. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that a majority of polymer blends require a compatibilizer in order to achieve a synergism in properties.¹⁻⁹ These compatibilizers are polymeric in nature, spanning the interfacial region between otherwise strongly phase-separated polymers. These compatibilizers are typically formed during melt processing, i.e., the blending step.¹⁰ This mode of formation is a solventless process and economic, and, in addition, the compatibility is formed *in situ* between the two phases. As a result of its location, the compatibility is immediately available to lower surface tension, promote interfacial adhesion, and lower the domain size of the dispersed phase. Markedly improved stress-strain properties result. Although this mode of blend formation is highly desirable, the procedure is limited to the number of commercially available polymers capable of being utilized under reactive processing conditions.

Recently, a synthetic procedure was developed to incorporate low levels of oxazoline functionality onto styrene-acrylonitrile (SAN) copolymers. It was noted that oxazoline groups are reactive toward a

relatively wide range of functional groups. As a result, the utility of SAN copolymers as a blend compatibilizer should be substantially broader.

In this report, we detail the oxazoline functionalization of a broad range of laboratory-synthesized and commercially available (i.e., preformed) polymers containing nitrile groups. These families of materials include thermoplastics (SAN copolymers) and rubbers (nitrile rubbers, hydrogenated nitrile rubbers, and liquid rubbers). The former copolymers include styrene-nitrile copolymers which include random copolymers of SAN, alternating copolymers of SAN (alt-SAN), and random copolymers of styrene-methacrylonitrile (SMAN), while the latter systems include random copolymers of butadiene-acrylonitrile (NBR) and their hydrogenated analogs (HBNR).

EXPERIMENTAL

Styrene-acrylonitrile (SAN) copolymer with 25 and 30 wt % of acrylonitrile (SAN-25 and SAN-30) were purchased from Aldrich. Lustran® (Monsanto), a SAN copolymer with 30 mol % acrylonitrile, or SAN-18 was used as received. Paracryl CLT and BPLT (Uniroyal Chemicals) butadiene-acrylonitrile copolymer (nitrile rubber), contained 40 and 30 wt %, respectively, of acrylonitrile. Nipol 1312

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(Zeon Chemicals), a low molecular weight butadiene-acrylonitrile copolymer (liquid nitrile rubber) contained 28 wt % acrylonitrile. ZETPOL 2010 (Zeon Chemicals) contained 44% acrylonitrile (56 wt % butadiene) with 95 mol % of the double bonds hydrogenated, and ZETPOL 1010 contained 36 wt % acrylonitrile (64 wt % butadiene) with 95 mol % of the double bonds hydrogenated.

Therban 1701 possessed 34 wt % acrylonitrile and 100% of double bonds hydrogenated, and Therban 1701 SHRD possessed 34 wt % acrylonitrile and 96% of double bonds hydrogenated and were obtained from Mobay Chemicals. The reagents and solvents employed in this study were used as received (Aldrich Chemical). Zinc chloride was dried in a vacuum oven at 110°C for 2 days. ¹H-NMR spectra were obtained from a 300 MHz Varian XL-300 instrument.

Preparation of Alternating Styrene-Acrylonitrile (Alt-SAN) Copolymers

Alt-SAN copolymers were prepared according to Gaylord's procedure.¹¹ Typical reaction conditions used a molar ratio of styrene:acrylonitrile:zinc chloride of 1.0 : 1.0 : 0.1. The reaction was conducted under a nitrogen atmosphere at 55°C for 1.5 h with continual agitation. The resulting polymer product was repeatedly (typically three times) dissolved and precipitated in acetone and methanol. ¹H-NMR analysis indicated that the copolymer possessed a 0.9 : 1.0 molar ratio of SAN or 35% wt acrylonitrile content. The yield of copolymer was 9.5% by weight.

Preparation of Styrene-Methacrylonitrile (SMAN) Copolymer

The copolymer was prepared using 83.2 g styrene and 13.4 g methacrylonitrile at 60°C for 3 h with 0.3 g 2,2-azobisisobutyronitrile as the initiator. The resulting polymer solution was precipitated in a large excess of methanol. The copolymer was further purified by repeatedly dissolving and precipitating the polymer in acetone and methanol, respectively. ¹H-NMR analysis indicated that the copolymer was composed of styrene and methacrylonitrile with a molar ratio of 2.33 : 1.00. The yield of copolymer was 6.5% by weight.

Chemical Transformation of Nitrile to Oxazoline

A typical functionalization procedure for all the above copolymers (except Nipol 1313) is as follows: Dissolve 10 g SAN copolymer in 50 mL 1,2-dichloro-

benzene at 140°C. Subsequently introduce 4.8 g (78.7 mmol) 2-aminoethanol to the reaction mixture. When the temperature returns to 140°C, add 1.5 g zinc stearate (2.37 mmol). The reaction is maintained at this temperature for a predetermined reaction time. The reaction mixture is cooled and diluted with 50 mL chloroform. The resulting mixture is precipitated in 1 L methanol. The polymer is redissolved in 100 mL chloroform and again in 1 L methanol. The resulting polymer product was dried in a vacuum oven at 110°C for 48 h. For polymers containing an oxazoline content of more than 1 meq/g, the dissolving-precipitation procedure must be repeated at least one more time. Any trace amount of zinc stearate will cause crosslinking to occur.

Nipol 1312 is a liquid nitrile rubber and cannot be isolated through precipitation from methanol. The workup procedure entails mixing the reaction mixture with water and then collecting the bottom layer after centrifugation. The solution was dried over magnesium sulfate, and the oxazoline-functionalized nitrile rubber was obtained by distilling off the solvent under vacuum.

The oxazoline content was determined by ¹H-NMR using deuterated chloroform as the solvent. Triphenylmethane and naphthalene were used as internal standards for SAN copolymers and hydrogenated nitrile rubbers, respectively. The ethylene unit within the oxazoline moiety can be detected at δ 3.0–4.5. For a majority of monomeric oxazolines and pendant oxazoline groups located away from the chain backbone, the chemical shifts were found at δ 3.5–4.5.

RESULTS AND DISCUSSION

Thermoplastic Nitrile-Containing Copolymers

The chemical transformation of the thermoplastic copolymers were conducted under the conditions described in the Experimental section. The oxazoline content was determined by ¹H-NMR using triphenylmethane (δ 5.55 ppm) as the internal standard in comparison to the oxazoline at δ 3–4.5 ppm.¹² The specific results are shown in Table I.

An examination of the top three copolymer reactions in Table I shows that the acrylonitrile concentration has a marked effect on the extent of the oxazoline conversion. In this example, the weight ratio of copolymer to reactant concentration was invariant. Therefore, if the acrylonitrile concentration was the only dependent variable, the ratio of

Table I Chemical Transportation of Thermoplastic Nitrile-containing Polymers

Copolymers ^a	Reagent Ratio ^b	Reaction Time (h)	Oxazoline Content (meq/100 g)	Conversion Rate (meq/100 g/h)	100% Conversion (meq/100 g)
SAN-30	10 : 67 : 4.8 : 1.5	2.37	92.4	39.0	493
SAN-25	10 : 67 : 4.8 : 1.5	3.00	49.3	16.4	408
		3.90	64.5	16.0	408
SAN-18	10 : 67 : 4.8 : 1.5	1.50	12.9	8.6	294
		1.24	6.7	5.4	294
		5.70	39.9	7.0	294
		20.00	100	5.0	294
SMAN	10 : 67 : 4.8 : 1.5	15.00	9.9	0.7	286
SAN-30	0.5 : 13.4 : 0.48 : 0.25	4.20	96.7	22.0	493
Alt-SAN	0.5 : 13.4 : 0.48 : 0.15	6.02	111.3	18.5	529
		3.94	71	18.0	539

^a The number associated with the copolymer denotes wt % AN content.

^b Weight ratio of copolymer: 1.2 dichlorobenzene : 2-aminoethanol : zinc stearate.

^c Oxazoline content was determined by ¹H-NMR analysis.

^d Based on the complete conversion of all nitrile groups.

conversion for each SAN copolymer would be 30 : 25 : 18 or 1.67 : 1.39 : 1.00. However, the data show that the ratio is 39.0 : 16.2 : 5.8 (6.72 : 2.79 : 1.00). This difference in reaction kinetics is likely due to a "microenvironment" effect. In addition, all SAN copolymers were completely transparent, which indicates that the compositional drift is within a narrow range, i.e., approximately 3.5 wt % acrylonitrile content.¹³ It appears that the commercially available SAN copolymers are reasonably homogeneous in composition.

An analysis of the sequence distribution (assuming that monomer reactivity ratios for acrylonitrile and styrene are 0.04 and 0.41, respectively¹⁴) is presented in Table II. These values are obtained from monomer feed-copolymer composition relationships¹⁵ and from reactivity ratios.¹⁶ The results show that the probability of finding AN-AN-AN triads is negligible. The AN-AN-S triad for SAN 30, SAN 25, and SAN 18 are 4.86 : 2.36 : 1.00, respectively. When these ratios are combined with the appropriate acrylonitrile content ratios, the results (8.12 : 3.28 : 1.00) are consistent with the rate ratio for oxazoline conversion (6.72 : 2.79 : 1.00). Therefore, it appears that the triad sequences are also an important factor in the nitrile-to-oxazoline conversion. This phenomenon is further explained in the lower group of Table I, i.e., SAN 30 and alt-SAN. A direct comparison is made between a completely alternating and nonalternating copolymers, respectively.

Due to the high viscosity of the alternating SAN copolymer, a lower concentration of copolymer and a relatively high concentration of amine and catalyst was used. The results show that the average rate of oxazoline formation of SAN 30 is only slightly higher than that of the alternating copolymer. If the triad tacticity is the only cause of the "microenvironmental" effect, then the SAN-30 should be markedly more reactive. Based on this observation, the triad tacticity and nitrile content both are important factors influencing reaction kinetics.

Table II Relationship Among SAN Composition, Monomer Feed Concentration, and Copolymer Triad Distribution

AN Content	SAN 30	SAN 25	SAN 18
Wt % in polymer	30	25	18
Mol % in polymer	46	40	30
Mol % in feed ^a	62.1	42.9	23.1
Triad distribution ^b			
AN-AN-AN	0.38	0.0	0.0
AN-AN-S	11.52	5.66	2.37
S-AN-S	88.10	94.34	97.63

^a Monomer reactivity ratio is assumed to be 0.04 for AN and 0.41 for styrene. The mol % in feed was obtained from the equation $F_A = (\gamma_A f_A^2 + f_A f_S) / (\gamma_A f_A^2 + 2f_A f_S + \gamma_S f_S^2)$.

^b The distribution was calculated based on the probabilities of triad occurrence. See Ref. 15. S and AN denote styrene monomer units, and AN, acrylonitrile monomer units.

Table III Chemical Transformation of Nitrile to Oxazoline Units on NBR and HNBR

Nitrile Rubber	AN Content (Wt %)	Reagent Concentration ^a	Time (h)	Oxazoline Content ^b (meq/100 g)	Conversion Rate (meq/100 g/h)	Oxazoline Content ^c (meq/100 g)
Paracryl BPLT	30	10 : 134 : 3.2 : 1.0	24.0	45.4	1.9	448
Paracryl CLT	40	10 : 134 : 3.0 : 1.0	5.0	26.8	5.4	562
			2.0	10.0	5.0	
Therban 1701	34	10 : 134 : 3.2 : 1.0	15.8	24.5	1.6	495
Therban 1701 SHRD	34	10 : 134 : 3.2 : 1.0	24.0	52.8	2.2	495
Zetpol 1010	44	10 : 134 : 3.2 : 1.0	17.9	35.2	2.0	603
Zetpol 2010	36	10 : 134 : 3.2 : 1.0	10.9	22.4	2.1	518
NIPOL 1312	28	10 : 134 : 3.2 : 1.0	16.5	76.8	4.7	424

^a Weight ratio of nitrile rubber : 1,2-dichlorobenzene : aminoethanol : zinc stearate.

^b Oxazoline content was determined by ¹H-NMR analysis.

^c Based on the complete conversion of all nitrile groups.

Finally, it is noteworthy that relatively minor changes in structure can also be an important factor in the determining the rate of oxazoline conversion. A close examination of SAN 18 (30 mol % acrylonitrile) and SMAN (30 mol % methacrylonitrile) reactivity data shows that the former reacts approximately an order of magnitude faster than does the latter. It is likely that the increased steric hindrance of the chain backbone is responsible for the substantial drop in the reaction rate.

Elastomeric Nitrile-containing Copolymers and Their Derivatives

Butadiene-acrylonitrile copolymers (nitrile rubbers) are usually prepared by emulsion polymerization techniques. Due to different applications and sources, many nitrile rubbers were prepared with various degrees of crosslinking. Only a few nitrile rubbers were found to be completely soluble in 1,2-dichlorobenzene, which were subsequently used in this study.

It is noteworthy that, at a reaction temperature of 25°C, monomer reactivity ratios of acrylonitrile and butadiene are 0.02 and 0.39, respectively.¹⁷ In fact, this monomer mixture forms an azeotrope copolymer when the molar ratio of butadiene : acrylonitrile is 1.67 : 1.0, i.e., 37 wt % of acrylonitrile. Furthermore, two nitrile rubbers may be miscible even when the difference in acrylonitrile content is as high as 22%.¹⁸ This implies that, even with a substantial chemical composition drift during the course of polymerization, the resulting copolymer may have only one glass transition temperature, i.e., a miscible blend. Therefore, if the monomer reactivity ratios and compositions are available, calculation of the

feed ratio and monomer triad tacticity is not quantitatively meaningful.

The reaction conditions of the nitrile rubbers are similar to the example given in the Experimental section. Conversions were determined by using naphthalene as an internal standard, δ 7.3–7.9 ppm (2 quartets), in which its characteristic signal was compared to oxazoline at δ 3.5–4.5 ppm (two triplets).

In the top group of Table III, the results clearly show that Paracryl CLT (40 wt % acrylonitrile) reacted faster than did Paracryl BPLT (30 wt % AN). This difference in rate can be due to the difference in the AN-AN-S triad and nitrile content. However, this factor does not appear to be applicable with regard to the middle group of Table III, which is composed of hydrogenated nitrile rubbers. It seems that the reaction rates in these rubbers are not dominated by the acrylonitrile content. It is even more interesting that Nipol 1312 has the lowest acrylonitrile content (28 wt %), but possesses the same reaction rate as that of Paracryl CLT (40 wt % acrylonitrile). The reason for these variations are discussed in the next section.

Comparison of SAN and NBR-type Copolymers

As before, high solution viscosity of the nitrile rubbers was encountered and, consequently, the chemical transformation of nitrile rubbers was conducted at a polymer concentration of 10 wt %. For comparison purposes, two SAN copolymers, SAN-30 and SAN-25, were also conducted under similar conditions. The results are listed in Table IV.

It is important to note that SAN copolymers have substantially higher reaction rates than those of ni-

Table IV Chemical Transformation of Nitrile to Oxazoline Units on SAN Copolymers and Nitrile Rubbers

Polymer	Acrylonitrile Content (% Wt)	Reagent Ratio ^a	Time (h)	Oxazoline Content (meq/g)	Average Conversion (meq/h)
SAN-25	25	10 : 134 : 3.2 : 1.0	5.6	55.8	10.0
SAN-30	30	10 : 134 : 3.2 : 1.0	5.5	127.5	23.2
Paracryl CLT	40	10 : 134 : 3.2 : 1.0	5.0	26.8	5.4
Paracryl BPLT	30	10 : 134 : 3.2 : 1.0	24.0	45.4	1.9
Zetpol 2010	36	10 : 134 : 3.2 : 1.0	10.9	22.4	2.1
Therban 1701 SHRD	34	10 : 134 : 3.2 : 1.0	24.0	52.8	2.2
Nipol 1312	28	100 : 134 : 3.2 : 1.0	16.5	76.7	4.7

^a Reagent weight ratios: nitrile-containing polymers : 1,2-dichlorobenzene : 2-aminoethanol : zinc stearate.

trile rubbers, even though the SAN copolymers have lower acrylonitrile content. This observation implies that the comonomer (styrene or butadiene) as well as the solvent affect the reaction rate. It is well known that the dielectric constant of the medium strongly influences the rate of an ionic reaction.¹⁹ The close proximity of the comonomer undoubtedly aids in its ability to influence the kinetics of the nitrile-to-oxazoline transformation.

CONCLUSION

An investigation of the chemical transformation of nitrile to oxazoline on the SAN copolymer, nitrile rubbers, and their derivatives was conducted. For SAN copolymers, the triad tacticity influences the rate of oxazoline formation. The higher the AN-AN-S sequences, the higher the reaction rate. In addition, reaction rates dropped significantly when nitrile groups are adjacent to a bulky group (e.g., methacrylonitrile). It is also apparent that the dielectric constant of the comonomer can exert considerable influence on the nitrile-oxazoline transformation. The higher the dielectric constant of the comonomer, the higher the reaction rate. The results show that the reaction rates follow the series SAN copolymers > nitrile rubbers > hydrogenated nitrile rubbers. However, even with low reaction rates, reactive polymers comprising a broad range of nitrile-containing copolymers can be synthesized in a facile manner. As a result, a broad range of compatibilizers can be formed *in situ*, spanning thermoplastic-thermoplastic, thermoplastic-rubber, and rubber-rubber blend systems. The structure-property relationships of these families of blends are presently being investigated and will be the subject of a future publication.

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