Synthesis of Poly(\(N\)-acylethyleneimine)s

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**A B S T R A C T**

Using methyl 4-nitrobenzenesulfonate as an initiator and \(\sigma\)-dichlorobenzene as a solvent, decenyl (D) and heptyl (H) oxazolines monomers in ratio of 20/80 were copolymerized. Substitute oxazolines via ring opening copolymerization resulted in a random DH copolymer with a degree of polymerization of 100. Solution copolymerization as living cationic system is very sensitive to the presence of any trace of water in reaction vessel. Narrow molecular weight distribution was obtain by using purified chemical agents and well controlled copolymerization reaction. The copolymer can be considered as the poly(\(N\)-acylethyleneimine)s with allyl pendant groups randomly attached to the far end of their polymethylene side chains. Chemical structure and molecular weight of the polymer were characterized by NMR and GPC.

**Key Words:**
poly(\(N\)-acylethyleneimine)s; oxazoline; copolymer; living cationic polymerization.

**INTRODUCTION**

Ring-opening polymerization[1-3] and copolymerization [4-8] of 2-substituted alkyl oxazolines have been done by different research groups. The products of polymerization were hydorgel[4-9], liquid crystals [10], polymers, and copolymers with different chemical structures. Poly(\(N\)-acyl or \(N\)-aroylethyleneimine) can be made by the living cationic polymerization of 2-substituted oxazoline monomers [11-14]. The substituents can range from a small acyl group, e.g., acetyl or propionyl (polar \(t\)-
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amide polymers) through long chain acyls or aroyl (non-polar polymers which act like hydrocarbons groups with polar and/or ionic ends). Polymers with hydroxyl [15], allyloxy [16], acid [17], siloxane [18], and amine tails have been made [19]. These groups during the polymerization must be protected in order to stay unreacted and later when the polymerization proceed properly, they were revealed by hydrolysis. The backbone contains a t-amide function, thus the deprotection of the side chain without touching the backbone can be accomplished.

The synthetic versatility of oxazoline monomers allows us to tailor specific polymers. Many di-and tri-block copolymers, which have been used as very stable oil in water emulsifiers [19], water in oil emulsifiers [20-21], adhesive agents [22], and adhesives [23] have been made.

The polymerization chemistry of 2-substituted alkyl oxazolines is shown in Scheme I where, R can be a hydrogen, an aromatic or a heterocyclic group, an ester, an olefin, or a silicone moiety.

ω-Decenyl oxazoline and heptyl oxazoline from undecenylcy and octanoic acids, respectively are the cheapest monomers. These two monomers can be copolymerized to generate the decenyl/heptyl copolymer. poly(N-acylethylenimine) is a copolymer with allyl pendant groups randomly attached to the far end of their polymethylene side chains. The olefin group can be converted to polar functional groups such as hydroxyl group through several reactions [24]. The olefin group can also be transformed into epoxy [25] which can be hydrolyzed to a diol or reacted with SH- to generate a mercaptoethanol derivative. It can be reacted, also with imidazole to generate N-hydroxyethyl imidazole derivatives.

The functional groups would bind strongly to steel and in the best scenario, the crystalline polymer will coat the steel surface. Since it bonds strongly, water and other corrosion promoting species cannot delaminate the polymer coating from the metal surface. In addition, the reactive polymer surface can interact with other polymeric and non polymeric coatings.

In all cases, the final polar structure will be able to sit well on the surface of the crystallized lamella and coat the surface almost completely. Thus the surface is highly polar while the center is crystalline and non polar.

In this work, we have synthesized the decenyl/heptyl copolymer. The olefin groups in this copolymer will be transformed into epoxy and imidazole functional groups and will be reported in the coming paper.

EXPERIMENTAL

Materials
Methyl 4-nitrobenzensulfonate (Aldrich, 99%) was used as received and o-dichlorobenzene (ODCB) was purified by drying over P2O5 for 24 h while stirring and distilled at 179°C/760 mmHg using a spinning band column and stored under N2. Ethanolamine (Aldrich, 99%) was distilled at 170°C/760 mmHg through a spinning band column. Heptyl cyanide (Aldrich, 99%), undecylenic acid (Aldrich, 99%), ferrous chloride (FeCl2.4H2O, Fisher) and cadmium acetate (Pfaltz and Bauer, 99%) were used as received.

Instruments
The extent of reactions and purity of the compounds were monitored by a Perkin-Elmer gas chromatograph with a OV-17 phenyl silicon type column, running at 30°C/min heating rate from 80 to 320°C. As a solvent and an internal standard CDCl3 and TMS were used, respectively, when 1H NMR spectra on a XL-200, 200MHz FTNMR spectrometer were taken.

The molecular weight distribution was measured by gel permeation chromatography (GPC). The uncorrected number and weight average molecular weight were calculated using:

\[ M_n = \frac{\Sigma H_i}{\Sigma H_i / M_i} \]

and,

\[ M_w = \frac{\Sigma H_i M_i}{\Sigma H_i} \]
$H_i$ is the height of RI trace, measured at 0.1 mL interval and $M_i$ is the molecular weight obtained on the basis of the polystyrene calibration curve.

**Synthesis of Heptyl Oxazoline**

Heptyl oxazoline (H) was synthesized from heptyl cyanide via following the procedure in reference 26 (Scheme II). Cadmium acetate (Cd(OAc)$_2$, 6.0 g, 0.027 mol) and heptyl cyanide (C$_7$H$_{15}$CN, 195.0 g, 1.56 mol) were added into a 500 mL three necked round bottom flask. The solution was heated to 132°C. Ethanolamine (C$_2$H$_6$NOH, 190.0 g, 3.12 mol) was added while stirring the solution. A mole ratio (2:1) of ethanolamine to heptyl cyanide was used to get high conversion of the cyanide to oxazoline.

The reaction mixture was refluxed under N$_2$ at 135-140°C for 24 h. GC Analysis showed only two peak, i.e., all heptyl cyanide was transformed into heptyl oxazoline after 24 h while excess ethanolamine was left. The reaction mixture was then poured into 400 mL of cyclohexane. The phase containing the unreacted ethanolamine and other colored impurities was separated. A clear cyclohexane solution was obtained after decanting the colored ethanolamine phase. From the ethanolamine phase more monomer was extracted by cyclohexane (2×100 mL). The cyclohexane was removed by a rotary evaporator and the crude oxazoline was purified by spinning band distillation column at 93°C/2.7 τ (1 torr = 1 mmHg). Oxazoline was distilled into a flask with stopcock. After the distillation, the receiving flask was filled with dry N$_2$ and sealed by closing the stopcock.

GC Analysis indicated that the purity of the monomer was greater than 99.5%; the main impurity was unreacted heptyl cyanide. The product purity and chemical structure were checked by GC and $^1$H NMR (Figure 1).

**Synthesis of Decenyl Oxazoline**

Decenyl oxazoline (D) was synthesized by the following method [27, 28]. 91.62 g (1.5 mol) of Ethanolamin was mixed with 92.2 g (0.5 mol) of undecylenic acid in a flask connected to a spinning band distillation column. The mixture was refluxed for 8 h with the pot temperature at about 180°C. Then 9.17 g water (theoretical: 9.00 g) and 61.57 g of ethanolamine (theoretical: 61.08 gr) in excess were distilled through the spinning band column. Ferrous chloridehydrate (4.01 g, 3.5 w%) was added to the resulting yellowish hydroxyl amide melt. The mixture was heated under reduced pressure (about 10 mmHg). When the reaction mixture temperature was raised to nearly 200°C, the distillate which was a mixture of water and D monomer, was collected as rapidly as possible.

The distillate was extracted by cyclohexane (5×100 mL). The cyclohexane solution was stirred with anhydrous Na$_2$CO$_3$ and the solvent was removed by rotary evaporator. Clear and colorless D monomer of 99.0% purity was obtained. The purity was checked by GC. 3 g Anhydrous Na$_2$CO$_3$ was added to the above product. Decenyl oxazoline was distilled at 100-101°C/0.25 τ, (bp = 89°C/0.1 τ [29]), through a spinning band distillation column. The product purity and chemical structure were checked by GC and $^1$H NMR (Figure 2).

**Polymerization**

The copolymerization of heptyl and decenyl oxazolines was carried out in o-dichlorobenzene (ODCB) at 110°C. Methyl 4-nitrobenzenesulfonate (MeONS) was used as initiator (Scheme III). Freshly distilled decenyl oxazoline (D) (18.5 g) and Heptyl Oxazoline (H)
with 20/80 mole ratio were mixed with 55.5 mL ODCB in a three necked flasks under dry nitrogen gas and capped with rubber septa. After the monomers solution was heated to 120 $^\circ$C, 960 mg initiator (freshly prepared ODCB/MeONs solution) was injected. The polymerization progress was followed by GPC. Both D and H were consumed after 1 h. Polymerization was terminated by pouring the resulting viscous solutions into ethyl ether. After cooling, the polymer crystallized and formed gels. Polymer was washed with methanol (4×20 mL) four times to remove ODCB. The polymer was dried in a vacuum oven (50-60°C/0.1 τ) for 1 day. The purified polymer was characterized by GPC, and $^1$H NMR. The monomer ratio of synthesized polymer was nearly 20/80.

**RESULTS AND DISCUSSION**

Copolymerization of decenyl/heptyl copolymer (decenyl/heptyl abbreviated as DH) is a living cationic copolymerization system with an instantaneous initiation [30]. The polymer obtained had very narrow molecular weight distribution as demonstrated by its GPC results (Figure 3). Polydispersity indexes of DH copolymer based on polystyrene calibration indicates: $M_{\text{peak}} = 21676$, $M_n = 20732$, $M_w = 20757$ and their polydispersity index is about 1.01. The polymer with near total degree of Polymerization, 100 and narrow molecular weigh were synthesised. The polymer chemical structure was characterized by $^1$H NMR. In Figure 4 $^1$H NMR spectrum of copolymer is shown.

The differences in functional groups at the far end of the long polymethylene side chains do not change the monomer reactivity. The reason is that the structural differences of the monomers are located far away from the reactive site. Similarly, both heptyl and decenyl oxazolines have long polymethylene tails with a difference at their end (CH$_2$-CH=CH$_2$ vs. H) and it is
reasonable to assume that their copolymerization will generate a random copolymer.

CONCLUSION

A random copolymer, DH, with a total degree of polymerization of 100 and narrow molecular weight distribution was made by copolymerizing decenyl and heptyl oxazolines. The chemical structure and molecular weight distribution were determined by GPC and $^1$H NMR.

REFERENCES

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