

Novel, multifunctional unsaturated polyester polyols: synthesis and application

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Abstract

Caprolactone-based acrylated polyols are widely used in radiation curable coating formulations. The most commonly used such polyol contains two functional groups: acrylate and hydroxyl. The hydroxyl group reacts with (poly)isocyanates and other polyols to generate urethane, and the acrylate group makes the urethane radiation curable. This paper reports a new method to synthesize novel, multifunctional unsaturated polyester polyols in a one-step reaction and describe their applications in radiation curable flooring coatings.

Introduction

Unsaturated polyester polyols based on caprolactone have had wide application in radiation curing formulations since they were first developed in the early 1970s.¹ Only difunctional unsaturated polyester polyols, such as SR495 (Sartomer), are currently commercially available; however, multifunctional polyester polyols are highly desired to tailor coating performance. In this paper, we will review different synthetic approaches to make caprolactone-based acrylated polyols; introduce a new and efficient method to synthesize multifunctional unsaturated polyester polyols in a one-step reaction; and describe their application in radiation curable flooring coatings.

¹ U. S. Patent 3,700,643; U. S. Patent 4,632,975; U. S. Patent 4,390,565; U. S. Patent 4,639,499; U. S. Patent 5,731,406.

Experimental

Material: ϵ -Caprolactone was provided by Solvay (CAPA Monomer). 2-Hydroxyethyl acrylate was obtained from DOW. Trimethylolpropane diallyl ether (TMPDE), allyl pentaerythritol (APE) and trimethylolpropane monoallyl ether (TMPME) were provided by Perstorp. Pentaerythritol triacrylate (PETA) and dipentaerythritol hydroxyl pentaacrylate (DPHPA) were provided by Sartomer. Pentaerythritol diacrylate monostearate (PDAMS) was obtained from Aldrich.

General Synthesis Procedure: A 1500 mL flask was equipped with a stirrer, condenser, thermometer and nitrogen inlet and outlet tubes. 480 grams of ϵ -caprolactone were charged into the flask and stirred for 10 minutes with sparging nitrogen, then heated to 110 °C. A mixture of 0.70 grams monomethyl ether hydroquinone (p-methoxyphenol) and 476.85 grams trimethylolpropane diallyl ether (TMPDE) was added to the flask, followed by 1.03 grams stannous octanoate. After 10 minutes, the sparging nitrogen was changed to a nitrogen blanket. The reaction mixture was held for three hours at 110 °C, then cooled to room temperature, and the product was collected. The final product had a Brookfield viscosity of 85 centipoise at 25 °C, a APHP color of 25, a hydroxyl number of 112 and an acid number of 0.20.

Analysis Method: ¹H-NMR spectra were recorded on a Varian Unity 300 spectrometer at 300 MHz using CDCl₃ as a solvent and tetramethylsilane (TMS) as an internal reference. GPC analysis was run in duplicate on a Waters 150C instrument using an eight-column bank of μ Styragel columns with pore sizes 106, 105, 104, 103, 2(500), 2(100) Angstroms. A Refractive Index (RI) detector was used. The eluent was THF with a flow rate of 1.5 mL/min, and data was processed using Waters Millennium GPC software. Molecular weights (Mp) are based on polystyrene standards but the actual characterization of molecules is based upon their sizes in solution. Differential scanning calorimetry (DSC) was carried out with a TA Instruments 2910 DSC calibrated with indium. Initial and reheat DSC data were obtained by heating the specimens from -150 °C to 100 °C at a rate of 20 °C/min in a nitrogen atmosphere. The sample was quench-cooled using liquid nitrogen between the initial and reheat scans.

Results and Discussion

Part 1. Synthesis of multifunctional unsaturated polycaprolactone polyols

There are two synthetic routes reported to make multifunctional unsaturated polycaprolactone polyols. One reported that polycaprolactone polyols, triol or tetraol react with (meth)acrylic acid to produce a (meth)acrylated-capped polycaprolactone derivative with three or four functional groups.² Others reported that multifunctional unsaturated polycaprolactones can be made by reacting trimethylolpropane diallyl ether, 4,4'-diisocyanato-dicyclohexyl methane and polycaprolactone triol.³ Similarly, a composition was also reported that includes the reaction product of a polycaprolactone polyol, a multifunctional isocyanate, a lactone-acrylate adduct, and optionally, a hydroxyalkyl acrylate.⁴ These approaches all involve two step reactions, where the first step involves forming the polycaprolactone polyols and the second step involves modifying the end-capped hydroxyl groups to form the radiation curable groups by either (meth)acrylation or diisocyanate coupling reactions.

As we reported during the RadTech 2000 conference,⁵ ring-opening polymerization of caprolactone catalyzed by an organometallic compound in the presence of unsaturated alcohol provides a direct way to prepare unsaturated lactone-based polyols.

Ring-opening polymerization of lactones can be initiated by anionic, cationic, free-radical, active hydrogen, and coordination polymerization, etc., mechanisms. According to the proprietary catalyst we used in this study, we believe our reaction follows a coordination polymerization mechanism. Coordination ring-opening polymerization of lactone usually proceeds through an insertion mechanism, and the detail of the mechanism depends on the metal compound. For example, metal alkoxides containing free *p* or *d* orbitals of a favorable energy (Mg-, Sn-, Al-, Ti-, Zn-alkoxides) can be used as catalysts. In this case, a two-step insertion mechanism prevails. First, the lactone forms a complex with the initiator. The complex then undergoes a rearrangement of covalent bonds leading to the cleavage of the metal-oxygen bond of the initiator and the acyl-oxygen bond of the cyclic monomer. If a proper

² U.S. Patent 4,555,449; U.S. Patent 4,632,975.

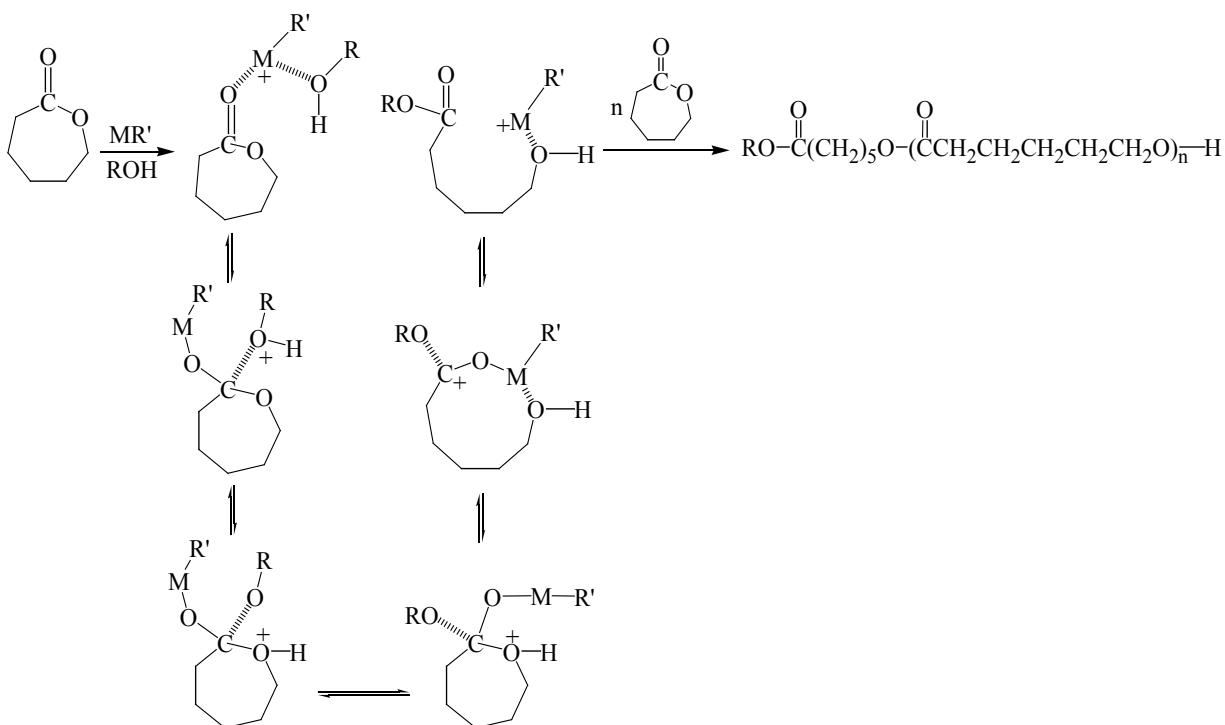
³ U.S. Patent 4,150,169.

⁴ U.S. Patent 4,618,635.

⁵ D. Tian, J. S. Ross and G. A. Sigel, "A Comparison of Caprolactone Based Polyols in Flooring Formulations", RadTech 2000, 251(2000).

initiator is used (i.e. Al-alkoxides), the ring-opening polymerization of lactones would be a "living" polymerization, which means that one can control the polylactone's molecular weight and molecule architecture (i.e., block, graft, comb, hyperbranched polymers) with narrow molecular weight distribution.^{6,7,8} When metal halides such as SnCl₂ are used, they act as Lewis acid catalysts in a ring-opening polymerization, actually initiated with active hydrogen compounds such as alcohol. Figure 1 shows its polymerization mechanism, in which MR' represents the catalyst (i.e., metal halides) and ROH could be alcohol or an alcohol derivative.

Figure 1. Polymerization Mechanism



Obviously, when 2-hydroxyethyl acrylate (HEA) is used as a hydroxyl-containing compound, α-hydroxyl-ω-acrylate polycaprolactone can be made (Equation 1). During the RadTech 2000 conference, we reported a combinatorial approach to the selection of catalyst, catalyst level and the best

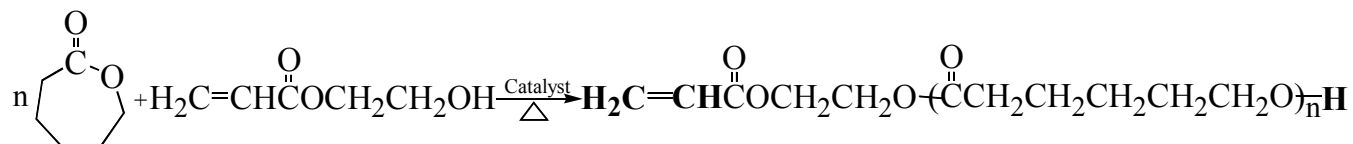
⁶ D. Tian, Ph. Dubois, R. Jerome, and Ph. Teyssie; "Macromolecular Engineering of Poly-lactones and Poly-lactides. 18. Synthesis of Star-Branched Aliphatic Polyesters Bearing Various Functional End Groups;" *Macromolecules*, 27, 4134 (1994).

⁷ D. Tian, Ph. Dubois, and R. Jerome; "Macro-molecular Engineering of Poly-lactones and Poly-lactides. 22. Copolymerization of ε-caprolactone and 1,4,8-Trioxaspiro[4.6]-9-undecanone Initiated by Aluminum Isopropoxide", *Macromolecules*, 30, 2575 (1997).

⁸ Dong Tian, Philippe Dubois and Robert Jerome, "Ring-Opening Polymerization of 1, 4, 8-Trioxaspiro[4.6]-9-undecanone : A Route to Novel Molecular Architectures for Biodegradable Aliphatic Polyester", *Macromolecular Symposia*, 130, 217 (1998).

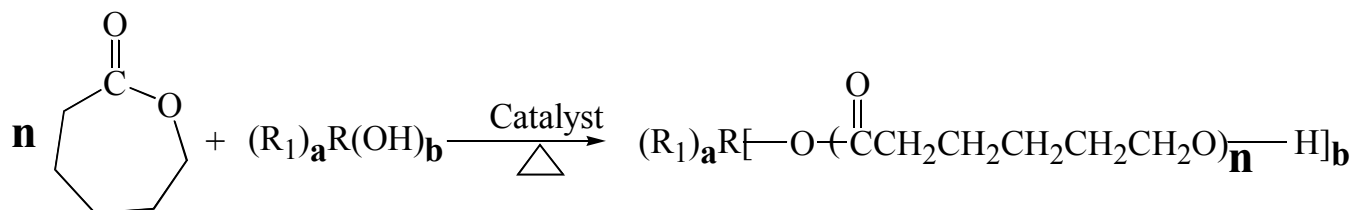
reaction conditions (e.g., temperature, time, etc.). According to Equation 1, changes in n , which defines the ratio of ϵ -caprolactone to HEA, alters the molecular weight of this type of unsaturated polycaprolactone polyol.⁹

Equation 1



According to the polymerization, a general reaction equation can be written (Equation 2). In this equation, a and b are, independently, equal to or greater than 1. R_1 is an olefin-containing moiety, examples of which include allyl, vinyl ether, vinyl, vinylidene, and (meth)acrylate, whereas R is an alkyl, aryl, aralkyl, alkaryl, ether or ester group, or substituted versions thereof. The n is the ratio of ϵ -caprolactone to $(R_1)_aR(OH)_b$, a hydroxyl and olefin containing compound. As we reported earlier^{8,9}, Equation 1 shows an example of difunctional unsaturated polycaprolactone polyols in which $(R_1)_aR(OH)_b$ is 2-hydroxyethyl acrylated, wherein a and b are both equal to 1.

Equation 2



Apparently, multifunctional unsaturated polycaprolactone polyols can be made when selected $(R_1)_aR(OH)_b$ has values of a plus b greater than 2. Examples of such reagents are, trimethylolpropane diallyl ether (TMPDE); allyl pentaerythritol (APE); trimethylolpropane monoallyl ether (TMPME); pentaerythritol triacrylate (PETA); dipentaerythritol hydroxyl pentaacrylate (DPHPA); and pentaerythritol diacrylate monostearate (PDAMS). Table 1 shows some examples of such multifunctional unsaturated polycaprolactone polyols along with reaction conditions and properties.

⁹ D. Tian, G. A. Sigel, K.M. Anspach and J. S. Ross; "The Effect of Polyol Molecular Weight on Properties of UV Curable Coatings – Experimental and Computational Results," RadTech Conference Proceedings; Indianapolis, IN; April 28–May 1, 2002.

Table 1. Summary of Synthesis of Multifunctional Unsaturated Polycaprolactone Polyols

ID	Arad1001	Arad1002	Arad1003	Arad1004	Arad1005	Arad1006	Arad1007
CL (gram)	480.00	620.00	550.00	60.00	50.00	62.50	420.00
TMPDE (gram)	476.85	307.97					
TMPME (gram)			399.81				
PDAMS (gram)				255.68	106.54		
DPPHA (gram)						136.63	
PETA (gram)							522.69
n value	2	4	2	1	2	2	2
a value	2	2	1	2	2	5	3
b value	1	1	2	1	1	1	1
Total Functionality, a+b	3	3	3	3	3	6	4
Reaction Temperature, °C	110	110	110	130	130	130	130
Reaction Time, Hour	3	8	3.5	14	14	9.5	7
Viscosity at 25°C	85	175	150	solid	solid	10,700	523
APHP Color	25	25	25	white	white	0	70
Hydroxyl Number	112	77	234	86	72	52	70
Acid Number	0.20	1.00	1.68	2.59	3.55	5.64	2.66

Arad 1001 and Arad 1002 both have linear structures and contain one hydroxyl at one chain end and two allyl ether groups at the other chain end. The difference between them is the ratio of ϵ -caprolactone and trimethylolpropane diallyl ether, which is 2 and 4, respectively. In other words, Arad 1002 has higher the molecular weight than Arad1001 or has two more ϵ -caprolactone repeat units in the macromonomer chain. Arad 1003 has a 2:1 ratio of ϵ -caprolactone and trimethylolpropane monoallyl ether, which is the same as that of Arad1001, but contains two hydroxyl groups at one chain end and one allyl group at other end. Arad1004 and Arad1005 both have linear structures and contain one hydroxyl at one chain end and two acrylate groups at the other chain end; however, Arad1004 contains one ϵ -caprolactone repeat unit whereas Arad1005 contains two ϵ -caprolactone repeat units in the macromonomer structure. Arad1006 contains five acrylates at one chain end and one hydroxyl group at the other chain end and two ϵ -caprolactone repeat units in the macromonomer structure. Some structures of multifunctional unsaturated polycaprolactone polyols are showed in Figure 2.

Figure 2. Selected Structure Examples of Multifunctional Unsaturated Polycaprolactone Polyols

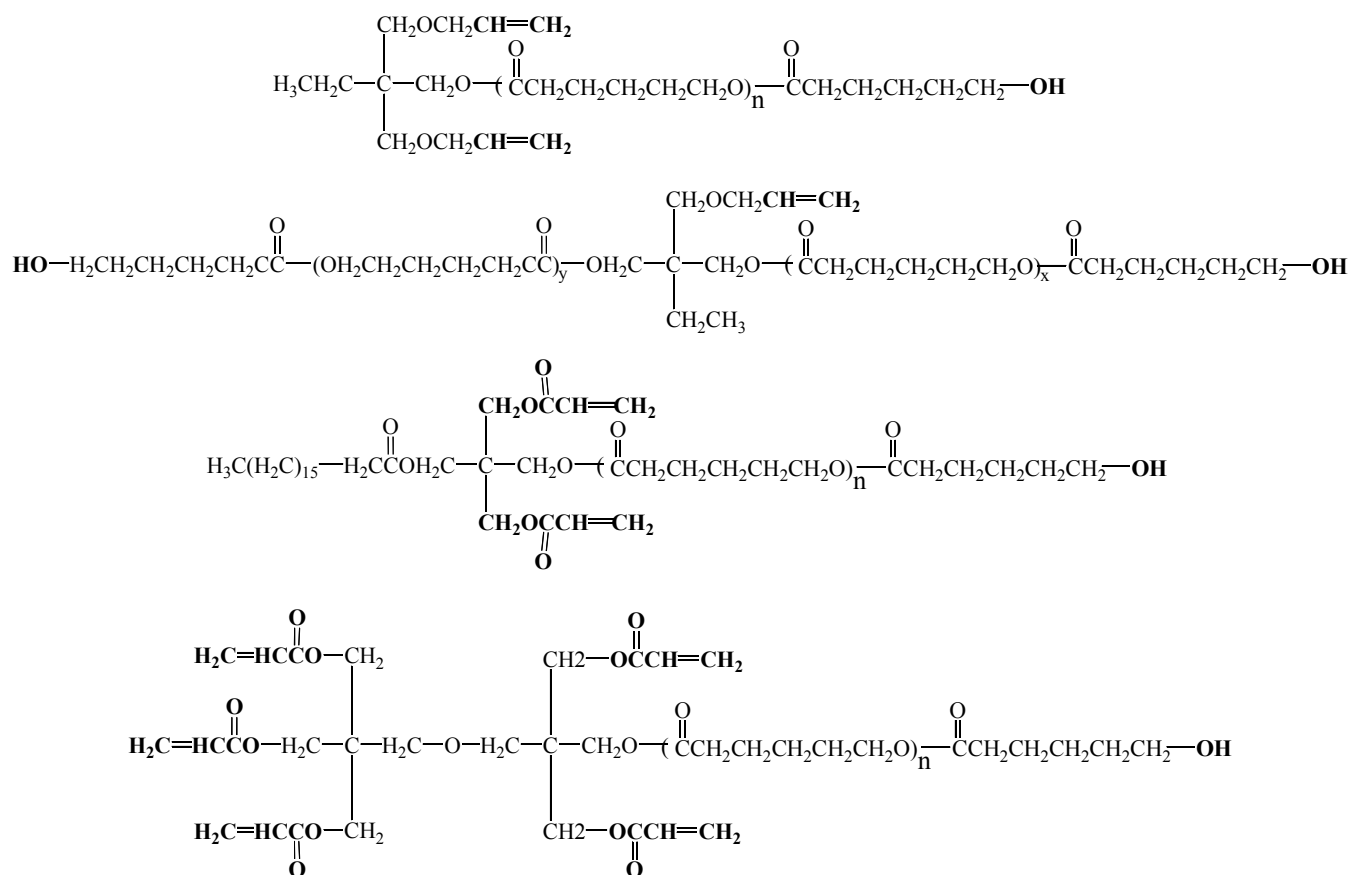


Figure 3 shows $^1\text{H-NMR}$ spectra of Arad1001 and TMPDE. It can be seen from the spectra that in the synthesis, the ϵ -caprolactone conversion was complete, but there was a residue of TMPDA in the final product.

Figure 4 shows GPC curves of Arad1004 and Arad1005. GPC analysis indicated that final multifunctional unsaturated polyols contain residue of unreacted PDAMS. Clearly, the higher ratio of ϵ -caprolactone and PDAMS, as seen in Arad1005 (B), results in higher molecular weight (cf. Arad1004, A).

Figure 3. ^1H -NMR Spectra of Arad001 and TMPDE

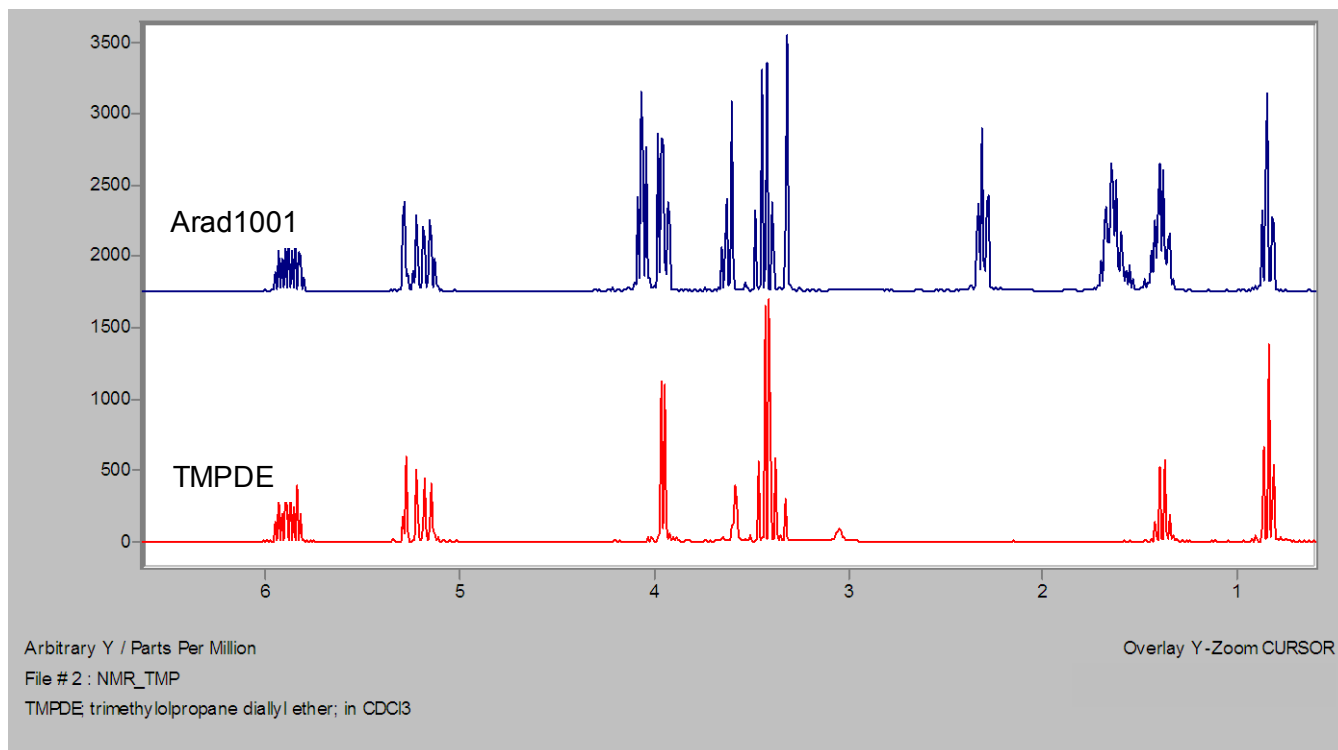


Figure 4. GPC Curve (Arad1004 black: A; Arad1005 red: B; PDAMS blue: C)

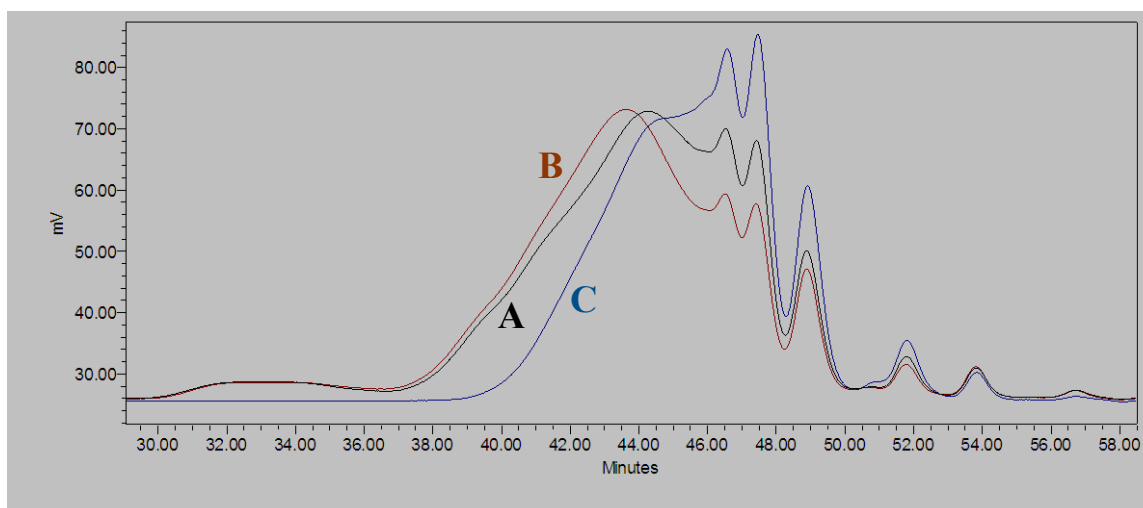
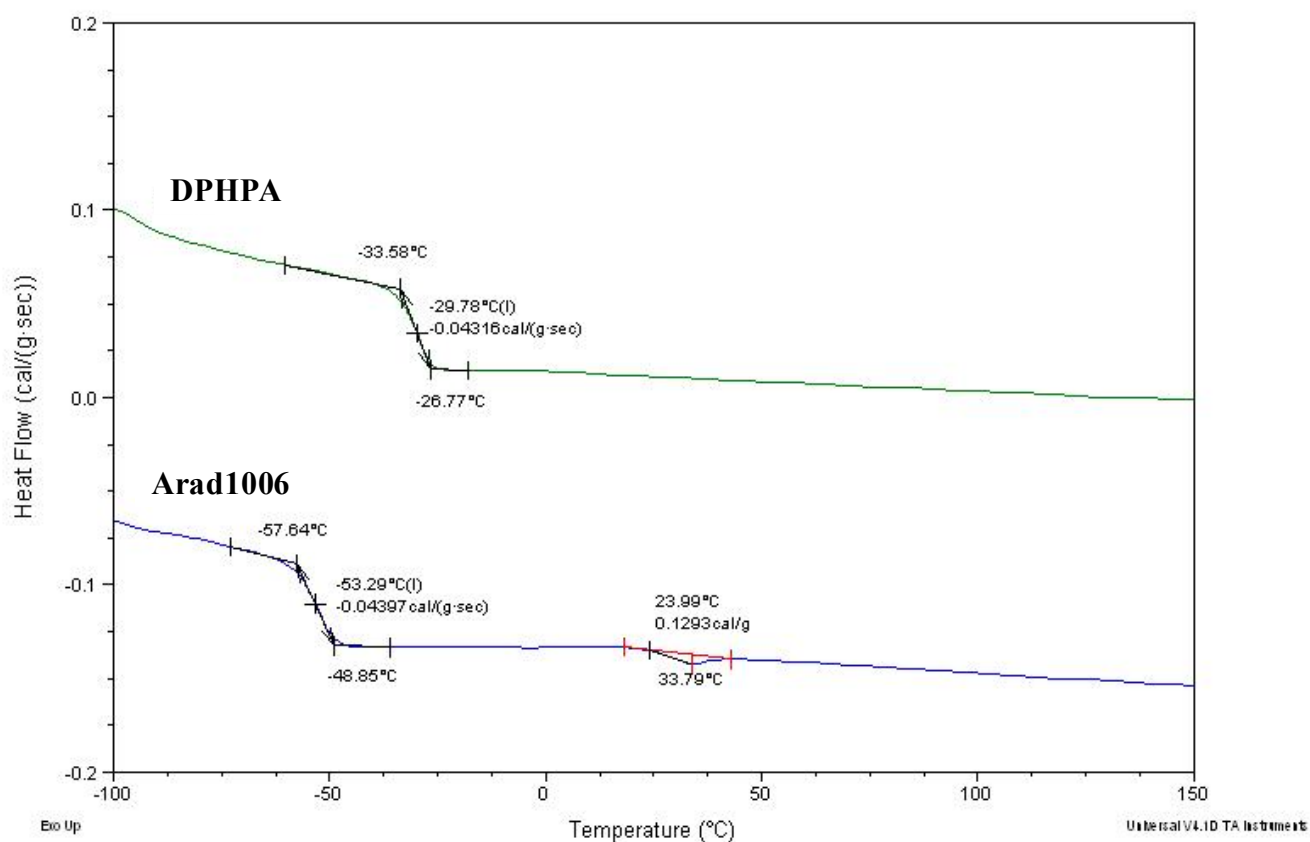


Figure 5 shows the comparison of the thermal properties of multifunctional unsaturated polycaprolactone polyol Arad1006 and DPHPA. The DSC trace of Arad1006 does not show a glass transition temperature (T_g) around -30°C that DPHPA exhibits. This indicates that DPHPA was converted into the macromonomer chain and chemically bonded, and the amount of residue of unreacted DPHPA in Arad1006 is not detectable by DSC analysis.

Figure 5. DSC Spectra of Arad1006 and DPHPA



Part 2. Application of multifunctional unsaturated polycaprolactone polyols in radiation curable flooring coatings

The four unsaturated polyols were selected and formulated into radiation curable floor coating compositions, respectively. The structures of the four unsaturated polyols are shown in Figure 6. The coatings were applied to vinyl flooring and UV cured. All coatings adhered well to the substrate.

Coating formulations are summarized in Table 2. In these formulations, coating 1 was used as the internal standard because it contained typical α -hydroxyl- ω -acrylate polycaprolactone (Arad100). The rest of the coatings contained multifunctional unsaturated polycaprolactone polyols (Arad1001, Arad1003 and Arad1007). The ratio of OH/NCO was kept constant when different multifunctional unsaturated polyols were substituted for Arad100. For the coatings #2, #3 and #4, the diisocyanate levels were kept the same as standard formula #1, and the polyol level was changed according to its molecular weight used in each formula. However, for coating #5, the polyol level was kept the same as standard formula #1 and the diisocyanate level was changed according to the molecular weight of Arad1007.

Figure 6. Structures of Unsaturated Polycaprolactone Polyols Used in the Floor Coating Formulations

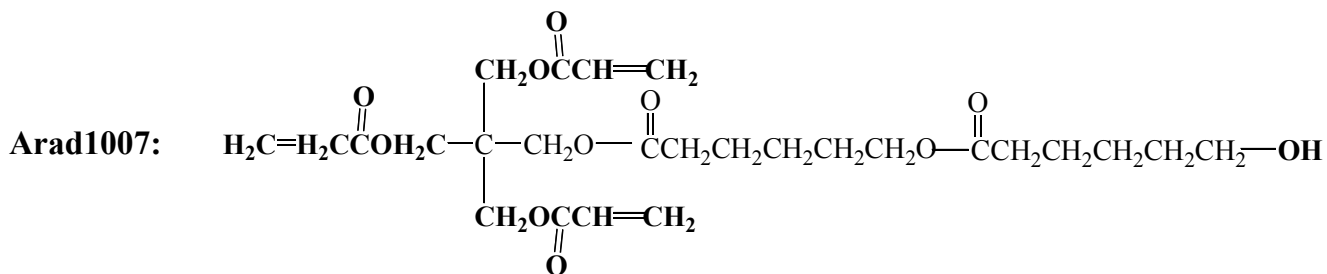
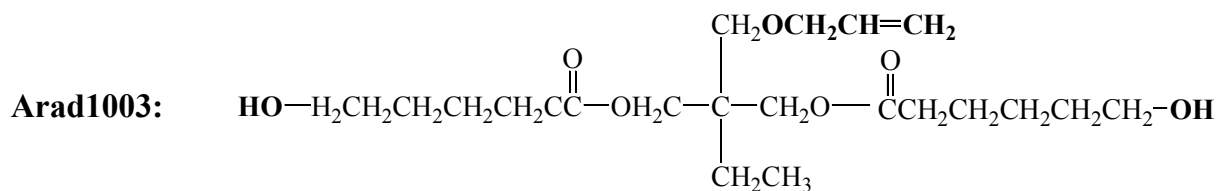
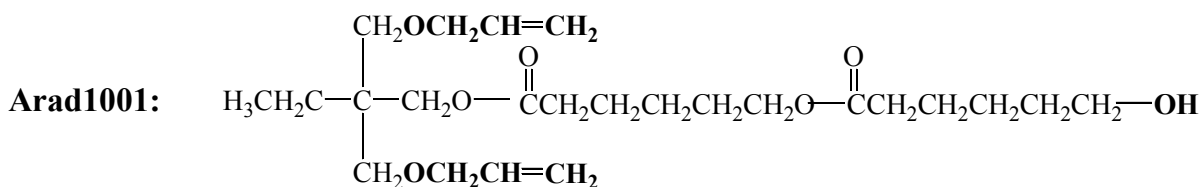


Table 2. Coating Formulations

Coating ID	#1	#2	#3	#4	#5
Ingredient	Amount (g)	Amount (g)	Amount (g)	Amount (g)	Amount (g)
Arad100	126.28	0	0	0	0
Arad1001	0	162.28	0	0	0
Arad1003	0	0	73.80	0	0
Arad1007	0	0	0	1029.76	126.28
Triacrylate Monomers	139.54	139.54	139.54	139.54	139.54
Polyester Polyols	34.38	34.38	34.38	34.38	34.38
Diisocyanate	59.17	59.17	59.17	59.17	19.59
Surfactant	0.93	1.02	0.79	3.26	0.83
Photoinitiator	3.60	3.96	3.07	12.64	3.20
Total	363.8943	400.35	310.75	1278.75	323.82

Property testing data for these coatings are summarized in Table 3. Compared with the floor coating comprising α -hydroxyl- ω -acrylate polycaprolactone Arad100, multifunctional polyol-containing floor coatings had better stain resistance, except for Arad1001. It is interesting to compare the structures of Arad1001 and Arad1003 (Figure 6) with respect to the effects of their structures on the coating stain resistance, gloss retention and coating break elongation (Table 3). Both Arad1001 and Arad1003 contain two ϵ -caprolactone repeat units, but Arad1001 contains two diallyl ether groups at one chain end and one hydroxyl group at the other chain whereas Arad1003 contains a monoallyl ether group grafted in the middle of the chain and both ends of the chain are end capped with hydroxyl groups. These structural changes resulted in better overall performance of the coating containing Arad1003 than that of Arad1001. Testing results of coatings #1, #2 and #4 indicated that the acrylate group probably is more active than the allyl ether group, and more acrylated groups would provide better stain resistance and gloss retention with decreased coating break elongation. Coating #4 contains more acrylate groups than the coating #5. It means that coating #4 should exhibit higher crosslink density than coating #5. However, coating #5 has better stain resistance than coating #4. The worse gloss retention value of

coating #5 also indicates that coating #5 seems to have higher crosslink density than coating #4. Research is under way to investigate this unusual floor coating behavior, and results will be reported in the near future.

Table 3. Coating Properties

Coating ID	Stain Resistance 1=best 5=worst	Gloss Retention 1=best 5=worst	Break Elongation
#1	4	1	24.2%
#2	5	5	10.3%
#3	3	2	32.4%
#4	2	1	7.0%
#5	1	3	6.8%

Conclusions

Novel multifunctional unsaturated polyester polyols can be made by a one-step reaction. The reaction involves ring-opening polymerization of lactone catalyzed by an organometallic compound in the presence of a multifunctional unsaturated alcohol via Coordination–Insertion mechanism. These novel multifunctional unsaturated polyester polyols can be used in radiation curable coatings and inks. As a case study, these multifunctional unsaturated polyester polyols were formulated as UV curable floor coatings. The floor coatings containing multifunctional unsaturated polyester polyols showed enhanced physical properties.

Acknowledgments

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