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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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Synthesis of Graft Copolymers from Diallyldimethylammonium Chloride and Acrylamide

Yun-Qing Lin^a; George B. Butler^a

^a Center for Macromolecular Science and Engineering and Department of Chemistry, University of Florida, Gainesville, Florida

To cite this Article Lin, Yun-Qing and Butler, George B.(1989) 'Synthesis of Graft Copolymers from Diallyldimethylammonium Chloride and Acrylamide', *Journal of Macromolecular Science, Part A*, 26: 4, 681 – 692

To link to this Article: DOI: 10.1080/00222338908052002

URL: <http://dx.doi.org/10.1080/00222338908052002>

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SYNTHESIS OF GRAFT COPOLYMERS FROM DIALLYLDIMETHYLAMMONIUM CHLORIDE AND ACRYLAMIDE

YUN-QING LIN and GEORGE B. BUTLER*

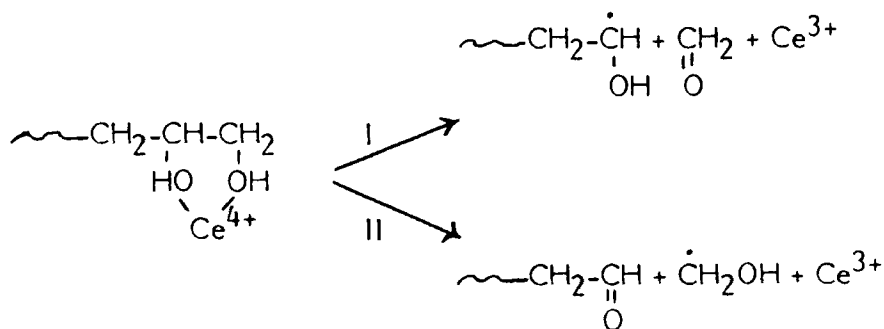
Center for Macromolecular Science and Engineering
and Department of Chemistry
University of Florida
Gainesville, Florida 32611

ABSTRACT

Previous results from this laboratory have shown that high molecular weight graft copolymers of acrylamide onto suitable copolymers of diallyldimethylammonium chloride and 2,3-dihydroxypropyl acrylate can be obtained by using ceric ion. However, homopolymer formation cannot be excluded since half of the radicals generated are not bound to the chain. In order to avoid homopolymer formation, a system was designed to lead only to generation of radicals covalently bonded to the chain. To this end, a novel copolymer substrate, diallyldimethylammonium chloride-co-3,4-dihydroxycyclohexylmethyl acrylate, was prepared. As an intermediate for this copolymer, 1-chloromethyl-*trans*-3,4-cyclohexanediol was synthesized. Studies of graft copolymerization of acrylamide and mixtures of acrylamide and diallyldimethylammonium chloride to this substrate are reported. Evidence that a higher ratio of consumed acrylamide is bonded to the substrate chain is based on a much higher ratio of \bar{M}_w to $[\eta]$ in these copolymers than in those derived from the substrate containing the 2,3-dihydroxypropyl group.

INTRODUCTION

We have reported the graft copolymerization of acrylamide (AM) onto copolymers of diallyldimethylammonium chloride (DADMAC) and 2,3-dihydroxypropyl acrylate in the presence of a ceric salt and nitric acid [1]. Copolymers of DADMAC and acrylic acid as the sodium salts were esterified with 3-chloro-1,2-propanediol (CPD), which was then used as the grafting site. Although CPD is a commercially available diol, there is a disadvantage for graft polymerization of vinyl monomers. As is well known, the disproportionation of the complexes formed by cerium(IV) with CPD can proceed by two routes:



According to the Route II case, formation of homopolymer of vinyl monomers cannot be excluded. On the other hand, the effect and efficiency of initiation of various alcohols in cerium(IV)-alcohol redox systems are very different [2]. In this work, in order to insure that the radical site can be generated only on the "prepolymer" chain and to establish a more proper and effective initiation system, a cyclic diol was synthesized. Graft copolymerizations of these new prepolymers of the diol with AM and monomer mixtures of AM and DADMAC were carried out.

EXPERIMENTAL

Materials

3-Cyclohexene-1-methanol (CHM) (98%, Aldrich Chemical Co.) was used as received. AM, commercially available reagent, was recrystallized from acetone. DADMAC, obtained from Allied Co. as a 60% aqueous solution of DADMAC, was used without further purification. Acrylic acid (AA)

(Eastman Kodak Co.) was distilled before use. Ceric ammonium nitrate (G. F. Smith Co.) was used without purification. All other products, such as thionyl chloride, acetic anhydride, hydrogen peroxide (30%), pyridine, and ether, were reagent grade or the equivalent.

Synthesis of 1-Chloromethyl-*trans*-3,4-cyclohexanediol

The synthesis of 1-chloromethyl-*trans*-3,4-cyclohexanediol (CMTCD) has not been reported. The procedure for its preparation is as follows.

A. Chlorination of CHM

The modified method of McKenzie and Tudhope [3] was used for chlorination of CHM. Thus, into a 200-mL three-neck flask, 33.7 g (0.3 mol) CHM and 33.2 g (0.42 mol) pyridine were added. Then 49.9 g (0.42 mol) thionyl chloride was added dropwise to the mixture, which was maintained at 60°C. After the reaction, water was added, and the oil (upper layer) was extracted with ether. The ethereal solution was washed with dilute hydrochloric acid, then with water several times, and finally dried over anhydrous sodium sulfate. After fractionation, a colorless liquid (1-chloromethyl-3-cyclohexene) (CCH), bp 43°C/5 torr, was obtained.

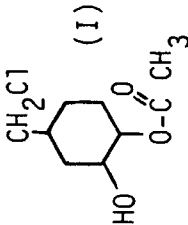
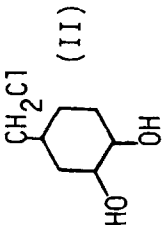
B. Hydroxylation of CCH

The method adopted is essentially that of Byers and Hickinbottom [4]. After hydrolysis of the oxidation product with a solution of KOH in 50% aqueous methyl alcohol, the product (bp 155-156°C/4.5 torr) was proven to be the monoacetate of the glycol by its IR spectrum and elemental analysis (Table 1). Then the same amount of KOH solution as that used in the first hydrolysis in water was added to the monoacetate. A solid product was obtained. It was then recrystallized from ethyl acetate.

Synthesis of Poly-DADMAC-*co*-Acrylate (prepolymer)

The method described in a previous paper [1] was used for preparing the prepolymers. Copolymerization conditions were modified as follows: The molar ratio of acrylic acid to DADMAC in the monomer feed was 1:20, the pH of the reaction mixture was 7, and the temperature of copolymerization was 50°C. The esterification of poly-DADMAC-*co*-AA by 1-chloromethyl-3,4-cyclohexanediol was carried out under the same conditions.

TABLE 1. Results of Identification for the Products of Hydroxylation of CCH^a

Sample	Molecular structure	Boiling point (5 torr), °C	Melting point, °C	Elemental analysis (%)		
				C	H	Cl
The product after 1st hydrolysis	 <p style="text-align: center;">(I)</p>	155-156	—	51.79	7.50	17.48
The product after 2nd hydrolysis	 <p style="text-align: center;">(II)</p>	—	107-108.5	51.23	7.89 (21.58)	21.64

^aTheoretical values for I and II are: C, 52.30%; H, 7.32%; Cl, 17.15%; and C, 51.07%; H, 7.96%; Cl, 21.53%; respectively.

Graft Copolymerization

The copolymerization was carried out according to Pledger et al. [5]. After 24 h the resulting copolymer was precipitated by adding the dilute reaction mixture dropwise to a large amount of acetone. The copolymer was then washed several times with small amounts of acetone and vacuum dried to constant weight at 40°C. Polymer yield was calculated by

$$\% \text{ yield} = \frac{(\text{g of polymer recovered}) \times 100}{(\text{g of prepolymer added}) + (\text{g of AM added})}$$

The copolymer sample for GPC and elemental analysis was purified by twice dissolving it in deionized water and reprecipitating it into acetone.

Intrinsic Viscosity

The viscosities of solutions of copolymers in 0.2 *M* aqueous Na₂SO₄ were measured with an Ubbelohde viscometer at 30 ± 0.2°C. $[\eta]$ was obtained by extrapolation of both reduced viscosities, η_{sp}/c , and inherent viscosities, $\ln \eta_r/c$, to infinite dilution.

Molecular Weights of Copolymers

The molecular weights of the copolymers were obtained by using a Waters Associates Model 590 gel-permeation chromatograph equipped with a 757-UV detector calibrated with polyacrylamide standards. The following conditions were used. Columns: glycerated controlled-pore glass beads, 3017 and 1273 Å; mobile phase, 0.2 *M* sodium sulfate; flow rate, 6 mL/min. The following equation was used to calculate the molecular weight:

$$\bar{M}_w = (6.9215 \times 10^6) - (1.0008 \times 10^5 V_R),$$

where V_R is the retention volume in milliliters.

Elemental Analysis

Elemental analyses were conducted by Atlantic Microlab, Inc.

IR and NMR Spectra

IR spectra were recorded with a Perkin-Elmer 281 infrared spectrophotometer. $^1\text{H-NMR}$ 60 MHz spectra were taken on a Varian EM-360L spectrometer. D_2O or CDCl_3 were used as solvent, depending upon the solubility properties of the samples.

RESULTS AND DISCUSSION

Synthesis of 1-Chloromethyl-*trans*-3,4-cyclohexanediol (CMTCD)

CMTCD was synthesized according to the method described in the Experimental section. The product of reaction of CHM with thionyl chloride was usually obtained in good yield. However, it is important that the reaction temperature does not exceed 60°C . The higher the temperature of reaction, the more by-products that were produced. The oxidation of CCH with osmium tetroxide and potassium permanganate failed to yield the *cis*-diol under the condition used. The double bond of CCH was easily attacked by peracetic acid. Products of the reaction usually consisted of epoxide and hydroxyacetoxy compounds [6]. They may lead to complications during hydrolysis. The hydrolysis reaction was readily stopped at the stage of the monoacetate of the glycol, as shown by its IR spectrum and elemental analysis of the distilled product (Table 1). The white solid glycol was obtained after hydrolysis of the monoacetate. The $^1\text{H-NMR}$ spectrum, IR spectrum, and elemental analysis data are shown in Fig. 1, Fig. 2, and Table 1, respectively.

Graft Copolymerization with AM

In a previous article [1] we described and discussed the graft copolymerization of AM with certain prepolymers (poly(DADMAC-*co*-2,3-dihydroxypropyl acrylate)). However, as mentioned above, CPD, when used as the esterification agent, may lead to some homopolymer formation by initiation through the $\dot{\text{C}}\text{H}_2\text{OH}$ radical formed via Route II. For this reason, a novel cyclic diol (chloromethylcyclohexanediol, CMTCD) and a prepolymer containing the CMTCD diol function (poly(DADMAC-*co*-3,4-dihydroxycyclohexylmethyl acrylate)) were synthesized. Graft copolymerizations of this new prepolymer with AM were then carried out under conditions comparable to those used in the previous paper [1].

Table 2 shows data obtained at various Ce^{4+} salt concentrations with

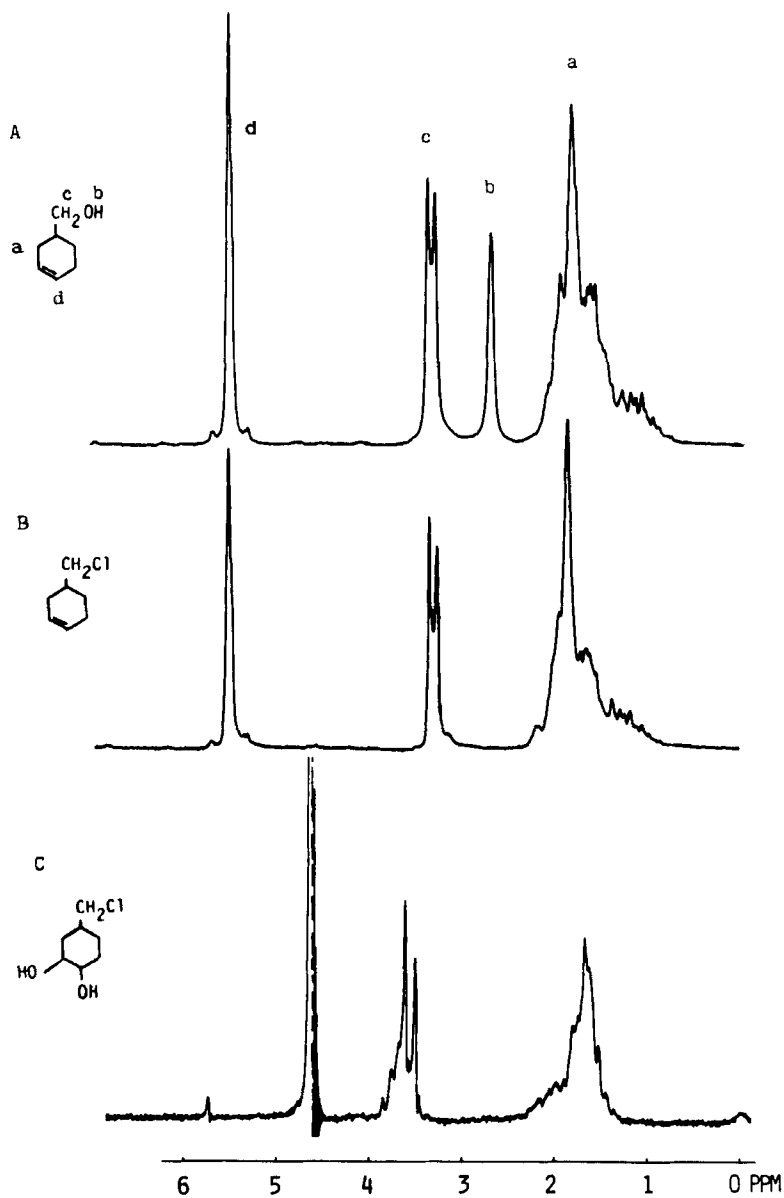


FIG. 1. $^1\text{H-NMR}$ spectra: (A) 3-Cyclohexene-1-methanol, CHM, in CDCl_3 ; (B) 1-chloromethyl-3-cyclohexene, CCH, in CDCl_3 ; (C) 1-chloromethyl-3,4-cyclohexanediol, CMTCD, in D_2O .

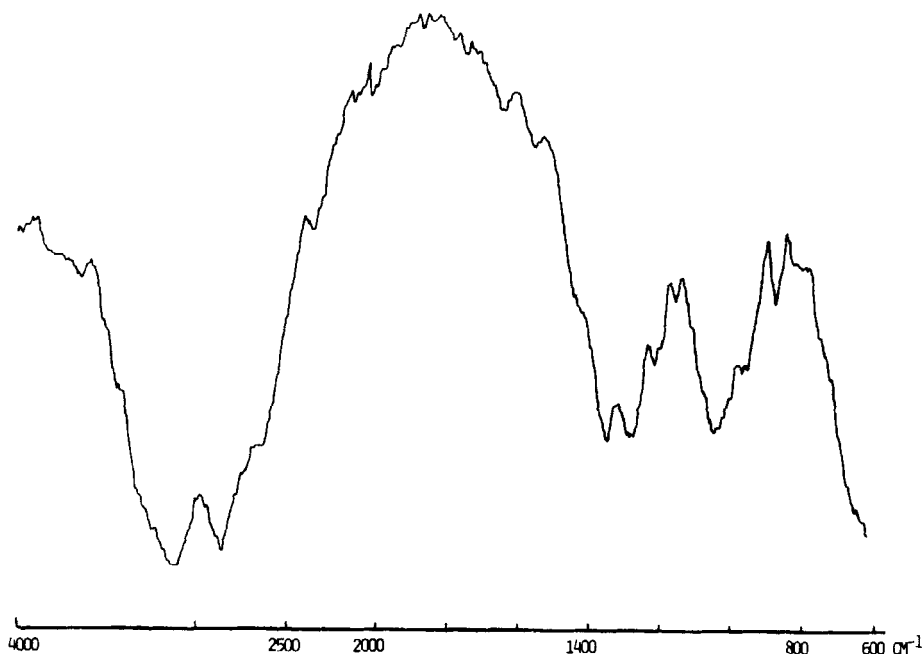
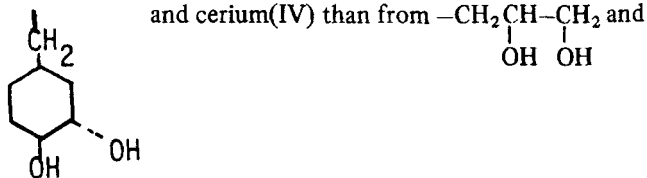


FIG. 2. IR spectrum of 1-chloromethyl-3,4-cyclohexanediol, CMTCD.

other conditions constant. It is evident that the conversions are very high for this series and the intrinsic viscosities are also quite high, especially at the low Ce^{4+} salt level. The activity of the prepolymer containing this *trans*-cyclic diol (CMTCD) for graft polymerization is superior to the CPD derived prepolymer (compare Tables 2 and 3). This may be because more stable complexes form from



cerium(IV).

Size exclusion chromatography (SEC) was utilized to characterize the graft copolymers (results in Table 2). The spectra of the unpurified samples usually contained two peaks. The peak with retention volume 72.3 mL was assigned to molecules of low molecular weight (prepolymer and monomer).

TABLE 2. Effects of Ce^{4+} Salt Level on Yield and Intrinsic Viscosity for Grafting onto Prepolymer from CMTCD (PP-5-1)^a

Run no.	$[\text{Ce}^{4+}]$, mmol/L	Yield		$[\eta]$, dL/g	$\bar{M}_w \times 10^{-4}$
		g	%		
DA-100	0.08	0.755	78.5	5.70	242
DA-101	0.10	0.776	80.7	5.55	233
DA-102	0.20	0.811	84.4	4.65	170
DA-103	0.30	0.740	77.0	4.35	146
DA-104	0.50	0.788	81.9	4.25	135
DA-105	1.00	0.695	72.3	3.66	116
DA-106	1.50	0.623	64.8	3.40	98

^aPolymerization conditions: Solution volume 25 mL, PP-5-1 0.252 g, AM 0.71 g, $[\text{HNO}_3]$ 4.5 mmol/L, temperature 30°C, polymerization time 24 h.

The molecular weights (\bar{M}_w) measured by SEC are also listed in Table 2. For comparison, the results of grafting to CPD-modified prepolymer are shown in Table 3. The different relationships between $[\eta]$ and \bar{M}_w in Tables 2 and 3 might suggest that CMTCD-produced macromolecules have more long side-branch chains. It has been well established that more highly branched high polymers usually have smaller $[\eta]$ than corresponding linear high polymers of the same total molecular weight. These results are in line with the fact that the CMTCD-modified prepolymers can provide more active radical sites on the chain than the CPD-modified ones. On the other hand, the \bar{M}_w s of products (at low Ce^{4+} level) of CPD were lower than those of CMTCD. This result might be due to the disproportionation via Route II. However, this point needs further proof, and future work is planned to check it.

Elemental analyses of the copolymers are listed in Table 4. With constant feed composition, the AM content of the copolymer remained almost constant, although $[\text{Ce}^{4+}]$ changed from 0.1 to 0.5 mmol/L. Also, the AM contents of the polymers were no longer equal to the AM in the feed, as might have been expected, but were much larger because the activity of the CMTCD-derived prepolymer (PP-5-1) was higher than that of the CPD-derived prepolymers (PP-2-2).

TABLE 3. Effects of Ce^{4+} Salt Level on Yield and Intrinsic Viscosity for Grafting onto Prepolymer from CPD (PP-2-2)^a

Run no.	$[Ce^{4+}]$, mmol/L	Yield		$[\eta]$, dL/g	$\bar{M}_w \times 10^{-4}$
		g	%		
DA-C-1	0.08	0.420	43.6	5.53	146
DA-C-2	0.10	0.662	68.8	7.35	152
DA-C-3	0.20	0.694	72.1	6.20	—
DA-C-4	0.30	0.661	68.7	5.92	148
DA-C-5	0.50	0.602	62.5	4.83	134
DA-C-7	1.00	0.514	53.4	4.20	124
DA-C-8	1.50	0.423	43.9	3.25	97

^aPolymerization conditions: Solution volume 25 mL, PP-2-2 0.252 g, AM 0.71 g, $[HNO_3]$ 4.5 mmol/L, temperature 30°C, polymerization time 24 h.

TABLE 4. Results of Elemental Analysis of Some Copolymer Samples^a

Sample no.	$[Ce^{4+}]$, mmol/L	AM in feed, wt%	Cl, wt%	N, wt%	AM in polymer, wt%
DA-101	0.10	73.9	2.73	16.80	85.8
DA-102	0.20	73.9	2.76	16.75	85.7
DA-104	0.50	73.9	2.76	16.70	85.6
DA-130	0.08	52.1 ^b	4.18	14.87	76.8

^aPolymerization conditions: Solution volume 25 mL, PP-5-1 0.252 g, AM 0.71 g, DADMAC 0.404 g, $[HNO_3]$ 3 mmol/L, Ce^{4+} 0.08 mmol/L, temperature 30°C, polymerization time 24 h.

^bMonomer feed also included DADMAC in the molar ratio AM:DADMAC = 4.

TABLE 5. Effects of $[\text{HNO}_3]$, on Yield and Intrinsic Viscosity^a

Run no.	$[\text{HNO}_3]$, mmol/L	Polymer, g	Yield, %	$[\eta]$, dL/g
DA-120	1	0.808	83.9	7.05
DA-121	2	0.761	79.1	6.95
DA-122	3	0.779	80.9	6.65
DA-123	4	0.721	75.0	6.80
DA-124	5	0.767	79.7	5.70
DA-125	6	0.625	64.9	5.65

^aPolymerization conditions: Solution volume 25 mL, PP-5-1 0.25 g, AM 0.71 g, $[\text{Ce}^{4+}]$ 0.1 mmol/L, temperature 30°C, polymerization time 24 h.

Graft Copolymerization with a Mixture of AM and Diallyldimethylammonium Chloride (DADMAC) Monomers

In order to introduce positive charges on the long side-branch chains and to modify the composition of the graft copolymers more effectively, graft copolymerizations of this new prepolymer with mixtures of AM and DADMAC were carried out. However, adding DADMAC to the polymerization system usually decreases the molecular weights of the products [7]. With the possibility of increasing the \bar{M}_w of the resultant copolymers, the experiments were conducted at low cerium(IV) levels. Table 5 shows that graft copolymers of AM having very high molecular weights can be obtained at $[\text{HNO}_3]$ below 3 mmol/L. Under these conditions, at molar ratio of AM: DMDAAC = 4, a graft copolymer (DA-130, Table 4) with an intrinsic viscosity equal to 6.0 was prepared. The yield of graft copolymer was 58%. Elemental analysis of the copolymer (Table 4) indicated a sharp increase in DADMAC content, which shows that this method is a very effective means of modifying copolymer composition.

CONCLUSIONS

The synthesis of a novel cyclic diol has been studied. Though the oxidation of 1-(chloromethyl)-3-cyclohexene (CCH) with osmium tetroxide and potassium permanganate under a variety of experimental conditions failed to yield

the *cis*-diol, the double bond of CCH was easily attacked by peracetic acid to give the corresponding *trans*-diol (CMTCD). Studies of the graft copolymerization of acrylamide (AM) were carried out with CMTCD-derived and CPD-derived prepolymers under comparable conditions. It is concluded that the former is superior to the latter in activity of graft polymerization and can produce graft copolymers having more long side-branch chains. Copolymerization with a mixture of AM and diallyldimethylammonium chloride (DADMAC) monomers usually yields low molecular weight copolymers. However, at low cerium(IV) and HNO₃ levels, a copolymer with $[\eta]$ of 6 dL/g and higher DADMAC content can be obtained.

ACKNOWLEDGMENTS

We would like to thank the Division of Sponsored Research of the University of Florida for its financial support and Dr. Huey Pledger Jr. for valuable discussions.

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Received December 21, 1987

Revision received April 21, 1988