Polymer-Supported Quinuclidinyl Catalysts for Synthesis of Cyclopolymerizable Monomers via the Aldehyde−Acrylate Coupling Reaction†

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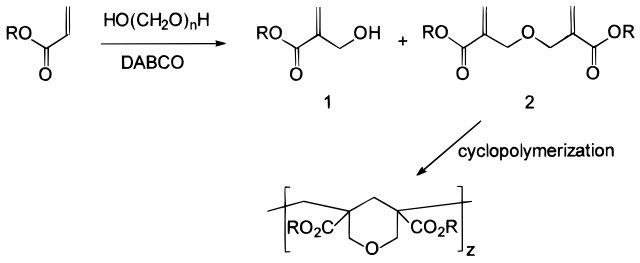
ABSTRACT: With an appropriate amine catalyst, formaldehyde addition to acrylates results in α-hydroxymethyl acrylate intermediates that undergo a further condensation reaction to provide ether-linked 1,6-diene monomers capable of efficient cyclopolymerization. While 1,4-diazabicyclo[2.2.2]octane (DABCO) is an effective catalyst in the synthesis of these cyclopolymerizable monomers, a series of polymer-supported amine catalysts were prepared and evaluated in an effort to further simplify this process. 3-Quinuclidinol was reacted with methacrylic anhydride to give the functionalized methacrylate monomer, which was copolymerized with methyl methacrylate and triethylene glycol dimethacrylate. Various polymerization techniques (bulk, solution, and suspension) were used to produce the cross-linked polymeric catalysts. Supports with mole fractions of catalyst ranging from 20% to 98% were examined. In reactions with ethyl acrylate and paraformaldehyde, certain polymer-supported catalysts gave near quantitative conversion to products. The rate of reaction with the polymeric catalysts was less than that of reactions with DABCO or other nonpolymeric model catalysts; however, after reaction times of 20 h, product yields and distributions were quite similar. With the polymeric catalysts, product isolation required only simple filtration or a solvent wash rather than an aqueous extraction step. This technique was also applied to the preparation of cyclopolymerizable resins containing multifunctional oligomers.

Introduction

The amine-catalyzed coupling reaction between acrylates and formaldehyde or paraformaldehyde provides α-hydroxymethyl acrylates **1** (Scheme 1).[1] The amine catalyst also promotes condensation between α-hydroxymethyl acrylates to form the ether-linked dienes **2**, which can be termed oxybis(methacrylates).[2−6] The 1,6-diene configuration in **2** provides a facile route for cyclopolymerization. Our primary interest in these novel monomers stems from the observation that highly converted polymers can be obtained with considerably less polymerization shrinkage than would be expected with conventional dimethacrylate monomers.[7−9] Additional potential advantages associated with the oxybis(methacrylate) monomers include low volatility and high polymeric glass transition temperatures. Unlike dimethacrylate monomers, the ester group functionality of the oxybis(methacrylates) can be varied to alter polymer properties. Bulky ester groups favor a highly efficient cyclization process, even in bulk polymerizations,[8] which leads to soluble linear polymers or polymers with low cross-link densities. Through the use of multifunctional oligomers containing these same 1,6-diene linking groups, highly cross-linked cyclopolymers with low polymerization shrinkage and good mechanical strength properties can be obtained.[9]

1,4-Diazabicyclo[2.2.2]octane (DABCO) has been used to accomplish the synthesis of oxybis(methacrylate) monomers from paraformaldehyde and a variety of acrylate esters. Other amine and phosphine compounds have also been evaluated as catalysts in the acrylate−aldehyde reaction. A sterically accessible bridgehead amine, such as in DABCO and quinuclidine, was found necessary for efficient production of the α-hydroxymethyl acrylate (αHMA) intermediate.[10] Although ease of synthesis with DABCO is already an attractive feature of the cyclopolymerizable oxybis(methacrylate) monomers, it was reasoned that the procedure could be simplified further by use of a polymer-bound version of the catalyst. In the present study, a polymerizable quinuclidine derivative was prepared and converted to a series of polymer-supported catalysts, which were evaluated along with other free-amine catalysts in the synthesis of α-hydroxymethyl acrylates and oxybis(methacrylates). The benefits expected from the use of a polymeric catalyst include (1) a simple filtration to remove the catalyst from the product (rather than an aqueous extraction that is often complicated by emulsion formation when product mixtures containing significant proportions of αHMA are involved), (2) a potentially solvent-free monomer production process, and (3) the possibility of catalyst recycling.

Scheme 1



Experimental Section

A mixture of 3-quinuclidinol (**3**, Scheme 2, 55 mmol), pyridine (275 mmol), and 2,6-di-*tert*-butyl-4-methylphenol (0.28 mmol) was cooled to 0 °C under argon. Methacrylic anhydride (110 mmol) was added dropwise, and the mixture

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† Certain commercial materials and equipment are identified in this paper for adequate definition of the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or that the material or equipment is necessarily the best available for the purpose.

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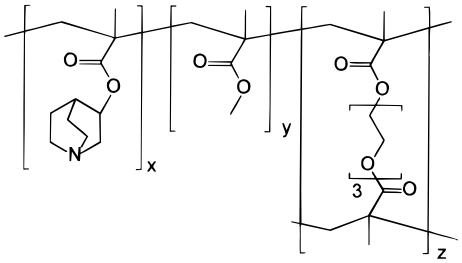
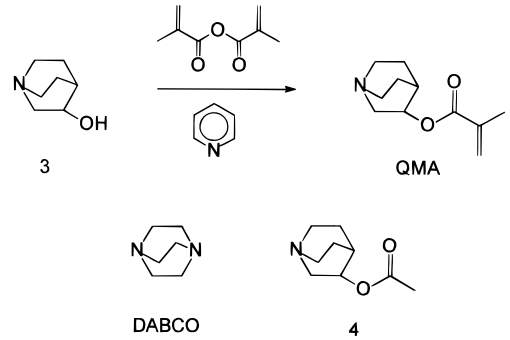


Figure 1. Cross-linked polymer network with pendant quinuclidinyl reactive sites for catalysis of the acrylate−aldehyde addition/condensation reaction.

Scheme 2



was heated under reflux for 4 h. Excess pyridine was removed under reduced pressure. The dark, viscous residue was diluted in chloroform (120 mL) and extracted with aqueous potassium carbonate. The organic layer was collected and dried over sodium sulfate. Evaporation of the solvent left a reddish-brown liquid residue that was fractionated by vacuum distillation to provide 3-quinuclidinyl methacrylate (QMA) as a colorless liquid (bp 74 °C/13 Pa; 64% yield). ^{13}C NMR: δ ($CDCl_3$) 18.1, 19.5, 24.3, 25.1, 46.3, 47.2, 55.4, 71.2, 125.2, 136.4, 167.0. An analogous method using acetic anhydride supplied 3-quinuclidinyl acetate (**4**)[11] as a nonpolymeric model compound.

A typical synthesis of an amine catalyst based on the solution polymerization of QMA is as follows: QMA (3.6 mmol), methyl methacrylate (MMA, 0.92 mmol), and triethylene glycol dimethacrylate (TEGDMA, 0.092 mmol) were combined in a mole ratio of 78:20:2 in toluene (0.8 mL). Azobis(isobutyronitrile) (AIBN, 0.025 mmol) was added to the monomer mixture, which was then heated at 65 °C for 18 h. The swollen polymer gel was extracted twice with warm chloroform to remove any unreacted monomer or soluble polymer. After removal of residual solvent in a vacuum oven (18 h/50 °C/200 Pa), the polymeric catalyst was obtained as a colorless, granular solid.

Equimolar amounts of ethyl acrylate (EA) and paraformaldehyde (PF) were combined with the polymeric catalyst (either 5% or 10% mole fraction based on quinuclidinyl equivalents in the copolymer) in a screw-capped vial. The neat reaction mixture was heated at 100 ± ca. 5 °C for 20 h. Integration over the vinylidene region in the ^{1}H NMR spectra of crude product mixtures supplied the extents of reaction and the product distributions that were used to evaluate the efficiency of the various catalysts.

Results and Discussion

While most polymer-supported catalysts are based on functionalized styrene/divinylbenzene networks,[12] MMA and TEGDMA were chosen here for copolymerization with QMA to form methacrylate-based polymer networks with pendant catalytic sites (Figure 1). It was reasoned that even in the absence of solvent, the methacrylate network should be compatible with the acrylic reactants and products involved in the cyclopolymerizable monomer synthesis. The ratio of monomers incorporated into the catalytic support is related to but not directly represented by the initial feed ratio. ^{1}H NMR analysis of a soluble copolymer prepared from QMA and MMA (20:80 mole ratio) showed that the content of QMA incorporated in the copolymer (mole fraction range of 18% to 24%) was similar to that introduced in the feed ratio. This correlation does not appear to hold at high QMA levels since the elemental analysis of a sample of the cross-linked polymeric catalyst prepared from a 78:20:2 mole ratio mixture of QMA/MMA/TEGDMA indicated a QMA content in the copolymer of only 66.5% (mole fraction). While actual catalyst concentrations may be somewhat less than those depicted by the feed ratios used in their preparation, throughout this study, all references to catalyst loading levels are based on the initial monomer feed compositions.

Table 1. Effect of Catalyst Preparation on Acrylate−Aldehyde Reaction[a]

catalyst preparation method	product distribution, %[b]				
	1	**2**	other	unreacted EA	**2**:**1**
bulk	17	48	8	27	2.8
suspension	10	30	6	54	3.0
solution	19	56	6	19	3.0
solution[c]	17	68	9	6	4.0

[a] Reaction conditions: 1:1 mole ratio of EA/PF with 5 mol % QMA/MMA/TEGDMA (20:78:2 mole ratio) polymeric catalyst heated at 100 °C for 20 h. [b] In crude reaction mixture based on acrylate equivalents with estimated relative standard uncertainty of ±2%. [c] Reaction time extended to 48 h.

Catalysts based on QMA/MMA/TEGDMA (20:78:2 mole ratio) were prepared by a variety of polymerization techniques using AIBN (mass fraction of 0.5%) at 65 °C for 18 h: bulk, solution (50% mass fraction in toluene), and suspension (4% mass fraction in water containing 0.8% (mass to volume) poly(vinyl alcohol)). The series of polymeric catalysts were employed in identical reactions with EA and PF to evaluate the effect of the catalyst preparation method on cyclopolymerizable monomer production. As shown in Table 1, the catalyst obtained by the solution polymerization procedure appeared to offer the best results in terms of minimum residual EA. Extension of the reaction time resulted in increased acrylate conversion and a higher proportion of the cyclopolymerizable 1,6-diene **2** in the product mixture. All subsequent work was performed with polymeric catalysts prepared by the solution polymerization technique. In an examination of the effect of QMA content in the copolymer on catalyst efficiency, it appeared that those catalysts with relatively high QMA contents are more effective (Table 2). Over the reaction time used here, polymer-supported catalysts with mole fractions of ≥78% QMA provided extents of reaction and product distributions quite similar to those available with the nonpolymeric catalysts.

The potential for catalyst recycling was explored by filtering one of the reaction mixtures and washing the retrieved polymeric catalyst with several portions of dichloromethane. The catalyst was then dried (18 h/50 °C/200 Pa) before reuse under the initial reaction conditions. As shown in Table 2, the product obtained through use of the recycled catalyst was deficient in **2** relative to the original reaction. Of the other products present, there was an elevated concentration of extended dienes (1,8-, 1,10-, etc.), which result from the coupling of multiple formaldehyde units to the acrylate prior to condensation.[5] Formation of these unstable acetal-fused dienes is favored during the early stages

Table 2. Effect of Catalyst Composition on Acrylate−Aldehyde Reaction[a]

catalyst composition	product distribution, %[b] 1	2	other	unreacted EA	2:1
Polymer-Supported Catalysts (QMA/MMA/TEGDMA)					
20:78:2	20	53	10	17	2.6
49:49:2	21	55	8	16	2.6
78:20:2	17	72	6	5	4.2
79.5:20:0.5	18	72	7	3	4.0
79.5:20:0.5[c]	17	55	19	9	3.2
98:0:2	19	67	8	6	3.5
Nonpolymeric Catalysts					
DABCO	18	75	6	0	4.2
3	18	74	8	0	4.1
4	21	70	7	2	3.3

[a] Reaction conditions: equimolar EA/PF with polymeric catalyst (mole fraction of 10%) heated at 100 °C for 20 h. [b] In crude reaction mixture based on acrylate equivalents with estimated relative standard uncertainty of ±2%. [c] Catalyst recycled from previous run.

Table 3. Removal of Product from the Catalyst[a]

catalyst QMA/MMA/TEGDMA (mole ratio in feed)	product yield, %[b] hydroxymethyl acrylate (**1**)	oxybis-(methacrylate) (**2**)	product ratio **2:1**
78:20:2			
neat filtration	10	45	4.5
$CHCl_3$ extract	7	17	2.4
total	17	62	3.6
97.5:0:2.5			
neat filtration	10	50	5.0
$CHCl_3$ extract	8	17	2.1
total	18	67	3.7

[a] Reaction of ethyl acrylate and paraformaldehyde (1:1 mole ratio) with polymer-supported catalyst (at mole fraction of 10% based on QMA content). The neat reaction was conducted at 100 °C for 20 h. [b] In product mixture based on initial acrylate equivalents with an estimated relative standard uncertainty of ±2%.

of the formaldehyde−acrylate reaction and with additional reaction time, they convert to the stable products **1** and **2**. Therefore, under appropriate reaction conditions, the polymer-supported catalysts should be suitable for recycling.

With increasing catalyst loading levels on the polymeric support, the overall amount of polymer necessary to achieve a constant effective catalyst concentration is reduced. For QMA mole fractions of <50%, the reaction mixture consisted entirely of a swollen gel phase. At high catalyst loadings (mole fractions of ≥78%), the relatively small amounts of the polymeric support used resulted in two-phase systems. There was little apparent difference in the degree of swelling observed for the catalyst cross-linked with TEGDMA at mole fractions of either 0.5% or 2.5%. In reactions with polymeric supports containing QMA mole fractions of ≥78% in the catalyst, a significant portion of the product could be press filtered directly from the neat reaction mixture. In all cases involving the supported catalysts, efficient product isolation required the use of a solvent, such as chloroform, to extract the product retained within the polymeric network. From the product distributions shown in Table 3, it is apparent that material collected by direct filtration has approximately half the αHMA content as subsequent product obtained by chloroform extraction of the remaining gel. This preferential retention of the more polar αHMA product in the polymeric catalyst raises the possibility of designing other monomers or catalytic supports that might further bias this affinity distinction and allow effective separation of the oxybis(methacrylate) and αHMA product components by simple filtration or solvent extraction.

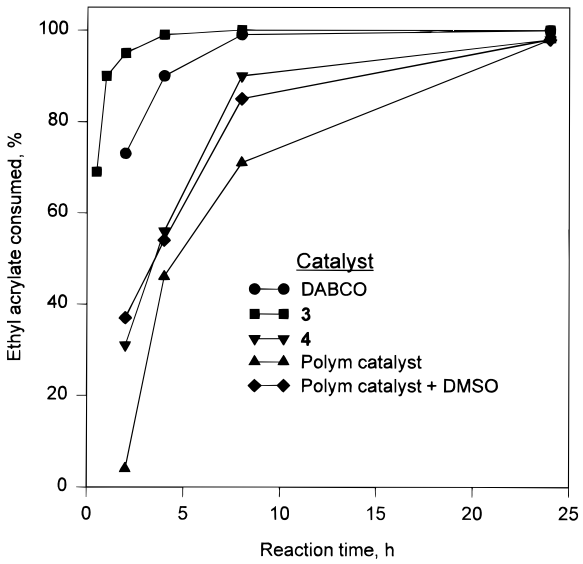


Figure 2. Rate of acrylate consumption in the equimolar reaction of ethyl acrylate and paraformaldehyde at 100 °C with the amine catalyst at a mole fraction of 10% based on amine content. The polymeric catalyst used was QMA/MMA/TEGDMA in a 79.5:20:0.5 mole ratio.

The rate of reaction with one of the polymeric catalysts (QMA/MMA/TEGDMA = 79.5:20:0.5 mole ratio) was compared with reaction rates obtained with the nonpolymeric catalysts: DABCO, **3** and **4**. As shown in Figure 2, DABCO was more efficient than the polymer-supported catalyst in promotion of the aldehyde addition to the acrylate. Addition of dimethyl sulfoxide (DMSO) as solvent (mass fraction of 50%) resulted in an increase in rate for the polymer-catalyzed reaction. However, inclusion of the polar solvent does not appear to favor formation of the oxybis(methacrylate) product since the ratio of **2** to **1** after 24 h was only 2.0. The model studies here verify prior findings of enhanced catalytic activity for 3-quinuclidinol (**3**) compared with DABCO in the formation of β-hydroxyalkenoates in similar reactions combining acrylates with alkyl or aryl aldehydes.[13] The improvement obtained with **3** is linked to the stabilization of the catalyst−acrylate adduct by hydrogen bonding. The current study demonstrates that the efficiency of **3** as a catalyst extends to reactions involving formaldehyde, which in addition to yielding αHMA, also proceed via amine-catalyzed etherification to produce the cyclopolymerizable oxybis(methacrylate) monomers. The increased rate observed for 3-quinuclidinol-catalyzed reactions relative to those with DABCO is emphasized by the analogous room temperature reactions, which provided 24 h ethyl acrylate consumptions of 53% and 4%, respectively. The acetate derivative **4** provided a reaction rate intermediate to that available with DABCO or the polymeric support. This indicates that the decrease in rate associated with the supported catalyst is due in part to catalyst structure (monoamine rather than diamine) and in part to constraints imposed by the polymer network (steric and diffusion effects). The reduced rate of reaction associated with **4** compared with **3** and DABCO is also in agreement with results previously obtained with substituted aldehydes.[14]

Scheme 3

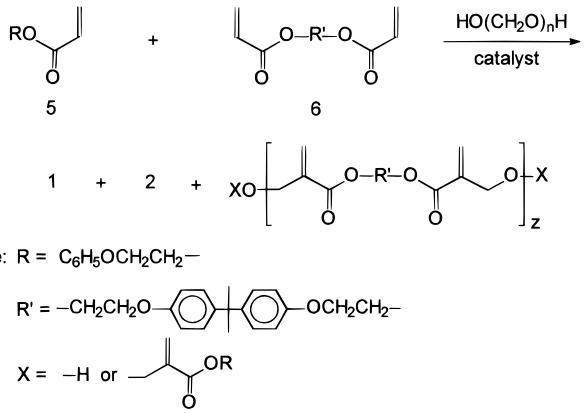


Table 4. Effect of Catalyst on Combined Monoacrylate/Diacrylate–Aldehyde Reaction[a]

catalyst	solvent[b]	unreacted acrylate groups, %	ratio of 1,6-diene to aHMA[c]
DABCO		0	8.2
polymer[d]		42	2.4
polymer[e]		33	2.6
polymer + DABCO[f]		0	6.2
polymer[d]	toluene	48	5.3
polymer	DMSO	0	18.7

[a] Phenoxyethyl acrylate (**6**) + ethoxylated Bisphenol A diacrylate (**7**, equimolar ratio) with a stoichiometric amount of paraformaldehyde and the catalyst (amine content of the catalyst at a mole fraction of 10% based on paraformaldehyde). Reaction conditions: 95 °C/24 h. [b] Mass fraction of 50% based on reaction mixture. [c] Mole ratio in acrylate equivalents as determined from the integrated ^{1}H NMR spectra. [d] Polymeric catalyst based on QMA/MMA/TEGDMA (79.5:20:0.5 mole ratio) was used. [e] Reaction time extended to 96 h. [f] Mole fraction of 10% was used for each catalyst.

In a variation of the general synthesis shown in Scheme 1, mono- and diacrylate starting materials can be combined in the DABCO-catalyzed reaction with paraformaldehyde to yield a cyclopolymerizable oxybis(methacrylate)/multifunctional oligomer resin system.[15,16] The monoacrylate reactant limits resin viscosity by generating low molecular weight diluent comonomer species and by acting as an end capper for the oligomeric product. An example of this approach is given in Scheme 3. With phenoxyethyl acrylate (**5**) and ethoxylated Bisphenol A diacrylate (**6**) used as the mixed acrylate reactants, the polymer-supported catalyst provides only partial conversion even after prolonged heating (Table 4). The use of DABCO as catalyst, either alone or in conjunction with the polymeric catalyst, results in complete consumption of the acrylate functional groups. With the polymer-bound catalyst used in the mixed mono/diacrylate reaction, addition of toluene as solvent retards the reaction compared with neat conditions while a polar aprotic solvent, such as DMSO, appears to greatly enhance conversion. In contrast to the relatively low oxybis(methacrylate) concentration present when DMSO was used in the polymer-catalyzed reaction with EA, an extremely high 1,6-diene content was observed in the product obtained from the DMSO-modified mono/diacrylate reaction. The increased formation of diene may indicate a greater extent of oligomerization of the diacrylate aided by DMSO swelling of the polymeric catalyst network. The enhanced level of 1,6-diene formation gives this material good potential for direct use as a resin capable of efficient cyclopolymerization with extensive cross-link formation. The techniques described here should also be well suited for use in the synthesis of water soluble cyclopolymerizable monomers and resins for which catalyst removal would otherwise be difficult.

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