Observations Related to the Amine-Catalyzed Coupling Reaction of Aldehydes and Acrylates

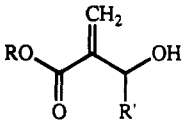
J. W. Stansbury

Dental and Medical Materials Group, Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received December 10, 1992
Revised Manuscript Received February 16, 1993

An amine-catalyzed Michael-type reaction has been applied to combine aldehydes and acrylates to yield α-hydroxymethylacrylates.[1] This reaction is of interest since it not only produces the reactive, functionalized α-hydroxymethylacrylate monomers such as **1** (Scheme I)[2] but, on closer inspection, it was found to give difunctional oxybis(methacrylate) monomers such as **2** as major products.[3-5] The difunctional monomers with the 1,6-diene orientation have a propensity toward polymerization by an alternating inter–intramolecular cyclization pathway. Multifunctional oligomeric monomers with the same 1,6-diene internal linkages have also been prepared.[5,6] Cyclopolymerization of these monomers introduces a tetrahydropyranyl repeat unit in the backbone of the addition polymer. The resulting cyclopolymers are generally characterized by high degrees of conversion,[7] high glass transition temperatures,[8] and low polymerization shrinkage.[7] The general synthesis allows the pendant ester groups in the difunctional monomers and the spacer groups in the multifunctional oligomers to be widely varied. This permits a large measure of control over properties of the resulting polymers. This paper highlights some observations associated with the synthesis and polymerization of monomers obtained by the aldehyde–acrylate coupling reaction.

The free-radical polymerization of methyl methacrylate occurs quite readily, while methyl α-ethylacrylate is nonpolymerizable under the same conditions.[9] This indicates a large steric effect associated with a β-substituent. However, a variety of esters of **1** undergo facile homo- and copolymerization in spite of the β-hydroxyl substituent. Even β,β-disubstituted acrylates, such as **6a** and **6b** (Figure 1) obtained from acetaldehyde (R′ = CH_3) and benzaldehyde (R′ = C_6H_5), have been found to polymerize, albeit reluctantly.[2] The homo- and copolymerizations of the ethyl esters of monomers **1**, **6a**, and **6b** reported here (Table I, 1% AIBN/65 °C/20 h) demonstrate that the β-hydroxyl group provides for excellent reactivity, while the additional alkyl or aryl β-substituent was responsible for the decreased polymerizability. The enhanced reactivity of **1** relative to methyl methacrylate is likely due to a combination of the polarity induced by the hydroxyl group as well as hydrogen bonding between the hydroxyl and carbonyl groups. The IR carbonyl absorption frequencies for methyl α-hydroxymethylacrylate and methyl methacrylate are 1718 and 1725 cm^{-1}, respectively.



6a ; R′ = CH_3

6b ; R′ = C_6H_5

Figure 1.

Table I. Polymerization of β-Hydroxyacrylates

	homopolymerization polymer yield,[a] %		copolymerization bulk, 1:1 with MMA[b]	
monomer	bulk	solution 10% in C_6H_6	polymer yield,[a] %	β-HA in polymer,[c] %
1, R′ = H	96	83	82	79
6a, R′ = CH_3	7	4	67	30
6b, R′ = C_6H_5	tr	tr	34	9

[a] Gravimetrically determined from twice precipitated polymer. [b] Equimolar ratio of methyl methacrylate (MMA) and β-hydroxyacrylate. [c] Mol % of β-hydroxyacrylate (β-HA) in the copolymer as determined from elemental analysis.

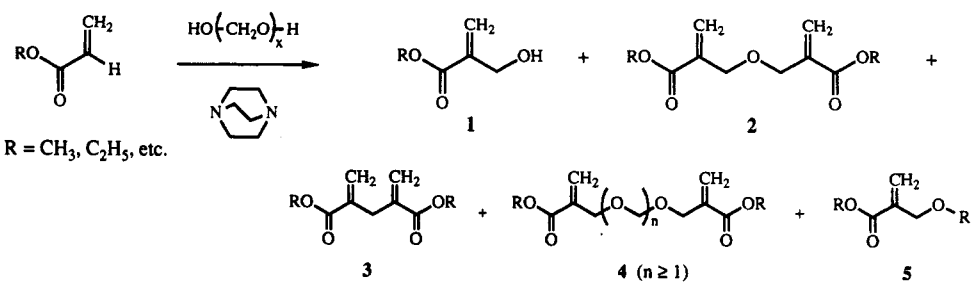
Table II. Effect of Reactants and Conditions on Product Distribution

	product composition,[a] %						
reactant/conditions	1	2	3	4	5	EA[b]	other[c]
formalin with 10 mol % DABCO[d]	32	34	0	21	3	10	
paraformaldehyde with							
1 mol % DABCO[d]	10	38	0	27	0	25	
10 mol % DABCO[d]	18	69	2	7	1	3	
100 mol % DABCO[d]	46	21	20	7	3	0	3
azeotropic removal of water[e]	6	87	3	1	1	0	2

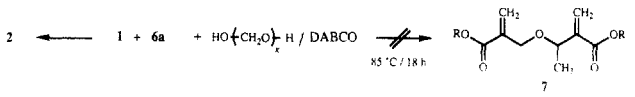
[a] Percentages are based on acrylate equivalents in the crude reaction mixture as determined from the integrated ^1H NMR spectra. [b] EA, unreacted ethyl acrylate. [c] Unknown. [d] 85 °C/20 h. [e] Same as d (10 mol % DABCO), then toluene added and refluxed for 2 h.

The DABCO-catalyzed coupling reaction of aqueous formalin or dry paraformaldehyde with an acrylate proceeds to yield both **1** and its condensation product **2** as well as other minor products (Table II). The use of paraformaldehyde favors the formation of **2**, and azeotropic removal of the water liberated by the etherification allows even greater yields of **2** to be attained. The concentration of DABCO significantly affects the reaction rate and the product ratio. The analogous reaction with acetaldehyde or benzaldehyde provided only the hydroxyacrylates **6a** and **6b**, respectively. No trace of the 1,6-diene condensation products or any other products was observed. The combination of **1** and **6a** in the presence of DABCO also failed to produce any of the asymmetric 1,6-diene **7** (Scheme II). An alternate asymmetric 1,6-diene **8**[10] (Figure 2) was prepared by the reaction of **6a** with methacryloyl

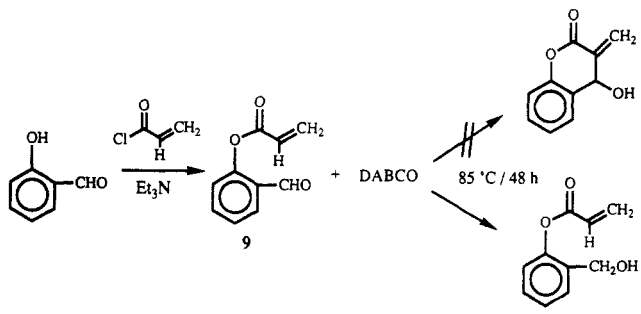
Scheme I



Scheme II

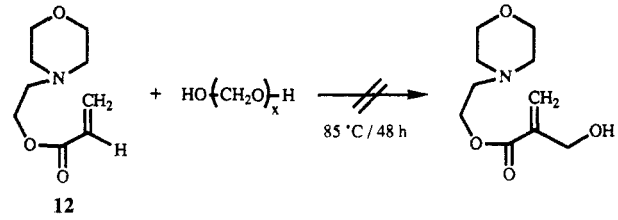


Scheme III



Scheme IV

Scheme V



chloride. Bulk polymerization of **8** yielded cross-linked polymer with a significant amount of residual unsaturation, which indicates inefficient cyclopolymerization. The additional β-substituent apparently inhibits the intramolecular cyclization as well as intermolecular addition and propagation through the more hindered double bond.

The intramolecular coupling of aldehyde and acrylate groups to produce hydroxyl functionalized α-methylene lactones was also investigated. The acrylate-substituted benzaldehyde **9** was synthesized from salicylaldehyde and acryloyl chloride (Scheme III). The attempted DABCO-catalyzed ring closure was unsuccessful with the acrylate-substituted benzyl alcohol isolated as the main product. The reduction may have occurred via a Cannizzaro reaction mechanism. A similar reaction utilizing the aliphatic aldehyde–acrylate **10** (derived from the acid-catalyzed condensation of 2,2-dimethyl-3-hydroxypropionaldehyde with acrylic acid) did provide the α-methylene lactone **11**[11] as the major reaction product (Scheme IV). Another type of intramolecular reaction was attempted with the acrylate and a cycloaliphatic tertiary amine incorporated in the starting material. Thus, 2-*N*-morpholinoethyl acrylate (**12**, Scheme V) was combined with paraformaldehyde; however, even after extended reaction times, no conversion to product was observed.

The restrictions imposed on the catalyst for the coupling of ethyl acrylate and paraformaldehyde were explored by varying the catalyst used. As shown in Table III, the more accessible tertiary aliphatic amines, quinuclidine and DABCO, produced the highest degrees of conversion to product. The use of arylphosphine catalysts gave relatively low yields of the α-hydroxymethylacrylate and diene products while the trialkylphosphine catalyst produced substantial amounts of the ethyl acrylate dimer **13** (Figure 3) which has been reported previously from similar reactions that did not include formaldehyde.[12]

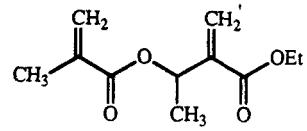


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Figure 2.

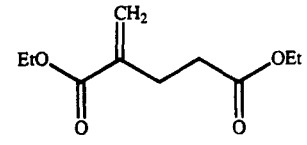

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Figure 3.

Table III. Catalyst Effect on Product Distribution

	product distribution,[a] %						
catalyst[b]	EA[c]	1	2	3	4	5	other
TEA	99	0	1	0	0	0	
QN	0	26	56	11	4	3	
DABCO	0	22	68	6	3	1	
DBU	95	1	4	0	0	0	
HMTA	96	1	3	0	0	0	
TPP	60	13	26	0	0	1	
TBP	50	3	3	0	0	2	42[d]
BDPPE	75	8	17	0	0	0	

[a] Catalysts were used at 10 mol %. Reaction conditions were 65 °C/96 h. Percentages are based on acrylate equivalents in the crude reaction mixture as determined from the integrated ^{1}H NMR spectra. [b] TEA, triethylamine; QN, quinuclidine; DABCO, 1,4-diazabibyclo[2.2.2]octane; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; HMTA, hexamethylenetetramine; TPP, triphenylphosphine; TBP, tri-*n*-butylphosphine; BDPPE, 1,2-bis(diphenylphosphine)ethane. [c] EA, unreacted ethyl acrylate. [d] Dimer of ethyl acrylate.

Acknowledgment. The contributions of Ms. Sonia Kim in the examination of the catalyst effects are gratefully acknowledged. This work was supported by Interagency Agreement 01-DE-30001 with the National Institute of Dental Research. 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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(10) Ethyl 3-(methacryloxy)-2-methylenebutyrate: ^{1}H NMR ($CDCl_3$) δ 1.30 (t, CH_2CH_3), 1.45 (d, $CHCH_3$), 1.96 (s, $=CCH_3$), 4.24 (q, CH_2CH_3), 5.58 (s, $=CH_E$), 5.77 (q, CHO), 5.81 (s, $=CH_E'$), 6.14 (s, $=CH_Z$), 6.29 (s, $=CH_Z'$).
(11) 4-Hydroxy-3-methylene-5,5-dimethyltetrahydropyran-2-one: ^{1}H NMR ($CDCl_3$) δ 0.78 and 0.87 (pair s, CH_3's), 4.0 (m, CH_2O and CHOH), 5.84 (s, $=CH_E$), 6.27 (s, $=CH_Z$).
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