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Acrylate-Containing Oligo(ether–ester) Cross-Linking Agents with Controlled Molecular Weights via End-Group Termination

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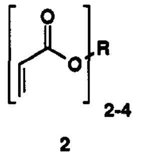
ABSTRACT: A novel new family of oligomers containing ether and ester groups in the backbone plus pendent vinylidine moieties was obtained through a straightforward and inexpensive reaction between bisacrylate esters and paraformaldehyde. The reaction was catalyzed by 1,4-diazabicyclo[2.2.2]octane. Initial formation of α-hydroxymethyl derivatives of the acrylate groups was followed by ether formation involving coupling of two of these groups. End-group analysis indicated variable molecular weights (depending on reactant ratios and reaction conditions) that were difficult to control. More important, higher oligomers underwent phase separation during attempted cross-linking of styrene, and gave nonuniform products with methyl methacrylate. Oligomer formation could be conrolled through the addition of ethyl or *tert*-butyl acrylate, which stopped the growing chains to give terminal ester units. These materials (at the 5% level) gave clear, hard, insoluble products with no phase separation for both styrene and methyl methacrylate bulk thermal and photoinitiated polymerizations. Incorporation at levels up to 50% was examined with methyl methacrylate. While rate of polymerization and gelation increased with increasing oligomer concentration, strength and toughness decreased. Characterization involved FTIR and solution ^{13}C NMR spectroscopies for reactive oligomers, and FTIR and solid-state ^{13}C CP/MAS NMR spectroscopies for insoluble products.

Introduction

Vinyl addition polymers enjoy widespread use in a variety of applications as thermoplastics. Ease of injection molding and low cost combine with good strength and toughness to provide a highly desirable combination of properties. Drawbacks to more universal use include creep, crazing, and solvent swelling and/or dissolution. These problems can be ameliorated to some extent through reinforcement and cross-linking. The latter is especially important in situations where maximum dimensional stability and strength are required. A variety of cross-linking agents are available commercially based on various structural topologies. The polymer of maleic anhydride and ethylene glycol (1) provides one example of an internally unsaturated cross-linker that is combined with styrene to form a matrix commonly used for glass fiber composites.[1] In contrast to backbone unsaturation are materials containing terminal acrylate groups (2). A number of such multifunctional acrylates are used as the major or only component in photocurable coatings,[2] dental composites,[3] and interpenetrating networks.[4]

$$\left[CH_2CH_2O_2C-CH=CH-CO_2 \right]_n$$

1



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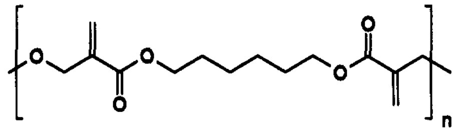
The topological approaches taken by 1 and 2 each have advantages. The former generates a more uniformly distributed network structure, and the latter provides much more rapid cure kinetics. It seems reasonable to attempt to combine these individual advantages into the same system; that is, one that contains evenly dispersed sites of unsaturation that are similar in structure and reactivity to the pendent acrylate groups. On the basis of a recently discovered ether-forming reaction (whose overall mechanism is given in Figure 1), we envisioned oligomerization of bisacrylate esters through methylene ether groups to give linear, multifunctional cross-linking agents of general structure 3. In fact, this approach was surprisingly facile as described in a preliminary communication.[5] Others have begun to explore this approach as well as evidenced by the recent presentations and preprints describing the chain extension of several diacrylates using this DABCO-catalyzed methylene ether formation.[6]



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In this paper we describe the conversion of several alkyl diacrylates to various oligomeric products through spontaneous ether formation of intermediate α-(hydroxymethyl)acrylate groups. The specific development of interest here is the use of acrylate monomers as end-capping agents to control molecular weight and incorporate reactive functionality at the chain ends. This synthetic approach provides a general pathway to a new family of multifunctional acrylates linked through backbone ether and ester groups. These materials possess excellent activity as cross-linking agents in photocurable systems and in bulk or solution polymerizations of vinyl monomers in general.

Experimental Section

All chemicals and solvents employed in the following procedures were used as obtained. All IR spectra were obtained with a Perkin-Elmer 1600 FTIR on KBr pellets for solid materials and as thin films on NaCl plates for liquids and oils. Solution ^{1}H and ^{13}C NMR spectra were acquired with a Bruker AC-300 using $CDCl_3$ as solvent and internal reference; tetramethylsilane was used as an additional internal reference on selected samples. Broadband ^{1}H decoupling was used with the latter for routine analysis along with off-resonance decoupling for determination of the number of directly bonded hydrogens. Solid-state ^{13}C

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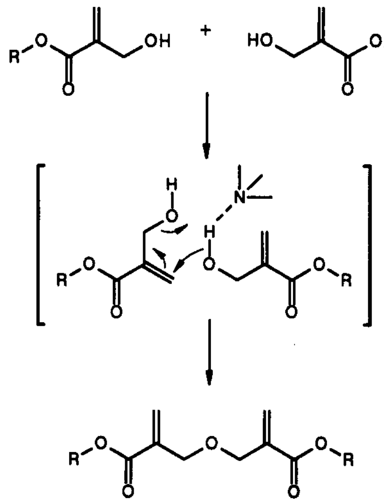

Figure 1. Overall mechanism for base-catalyzed ether formation involving α-(hydroxymethyl)acrylates.

NMR spectra of cross-linked products were obtained with a Bruker MSL-200 using standard acquisition parameters for rigid samples.

Diacrylate Oligomer Synthesis. A 1:1:0.2 functional mole-ratio mixture of 1.6-hexanediol diacrylate (HDDA, 50.6 g, 0.22 mol), paraformaldehyde (13.4 g, 0.44 mol), and DABCO (5 g, 0.044 mol) was placed in a 250-mL round-bottom flask fitted with a vigreux column and magnetic stir bar. The round-bottom was placed in an oil bath preheated to 65 °C, and the reaction stirred for 40 h. The cloudly suspension became a clear viscous liquid after 3–4 h and upon cooling formed a white solid. This product was filtered and dissolved in methylene chloride, which was then washed twice with aqueous HCl in a separatory funnel to remove DABCO. It is important that the water is made only slightly acidic (approximately 3–4 drops of concentrated HCl/400 mL of water) and that only a small amount of aqueous HCl is used for extraction. If the water is too acidic or too much is added, an emulsion forms that is very difficult to separate. The organic phase was then filtered through phase-separation filter paper to remove water droplets. Solvent was removed by rotary evaporation, and the product was placed under high vacuum to remove residual solvent. The yield was essentially quantitative, and this material was used as-obtained for polymerization and cross-linking studies.

Typical End-Capping Oligomerization. A mixture of the four reactive components in the mole ratio 1:2:4:0.8 (based on functional groups rather than molecules) was obtained by adding 1,6-hexanediol diacrylate (15 g, 0.066 mol) *tert*-butyl acrylate (16.99 g, 0.133 mol), paraformaldehyde (7.95 g, 0.265 mol), and DABCO (5.98 g, 0.053 mol) to a 100-mL round-bottom flask fitted with a vigreux column and magnetic stir bar. The flask was placed in an oil bath preheated to 70 °C, and the reaction mixture stirred for 90 h. The cloudy suspension became a clear, viscous liquid after 3–4 h and remained clear on cooling. Vacuum distillation (with added copper chloride as inhibitor) removed low molecular starting materials, byproducts, and catalyst. The pot residue often gelled, but extraction with CH_2Cl_2 and rotary evaporation gave the desired material, which was dried under vacuum. Remaining inhibitor was removed by passing a CH_2Cl_2 solution of the oligomer through acidic alumina followed by rotary evaporation. The crude reaction product could be used directly in polymerization and cross-linking evaluations. The ^{13}C chemical shifts of this product obtained in $CDCl_3$ (peak assignment as in Figure 3, ppm from TMS) are as follows: m, 165,6; l, 164.9; k, 138.8; j, 137.5; i, 125.3; h, 124.3; g, 80.7; f, 68.9; e, 64.5; d, 61.7; c, 28.6; b, 28.1; a, 25.7.

Similar procedures were carried out with varying ratios of the acrylate end-capper to approximately the same amounts of the other reactants. Yields of the relatively pure but crude reaction products ranged from ca. 50% to as high as 95% depending on the amount of spontaneous polymerization and cross-linking that occurred and on the amount of dimer of the end-capper formed as a byproduct and lost on workup.

Bulk Vinyl Monomer Cross-Linking Polymerization. The reactive oligomers were used to cross-link styrene and methyl methacrylate under bulk polymerization conditions using 0.5 wt % azobisisobutyronitrile (AIBN) as initiator at 65–70 °C. The amount of added oligomer was typically 5 wt %, although up to 50 wt % was used in some cases. At the lower concentrations of diacrylate oligomers, clear and homogeneous products were obtained that varied from extremely rigid to tough and slightly elastomeric due to swelling by residual monomer. None of the products would dissolve in common solvents for these polymers, although swelling was significant with some samples. At higher concentrations of cross-linking agent, turbidity developed early in the polymerization and phase separation was observed as the reaction continued. All samples were worked up by either drying immediately in a vacuum oven or by first extracting with solvent to remove residual monomer.

Photopolymerizations were carried out in small vials under a nitrogen atmosphere using Irgacure 651 (Ciba-Geigy; 2,2-dimethoxy-2-phenylacetophenone) as the photoinitiator. A 200-W UV light was situated ca. 12 in. from the vials to minimize heating effects. Samples were isolated and extracted with CH_2Cl_2 and dried in a vacuum oven before analysis.

Results and Discussion

We have recently examined the synthesis of alkyl α-(hydroxymethyl)acrylates (RHMAs)[7] and their conversion to ether dimers through a base-catalyzed dehydration.[8,9] These dimers serve as cross-linking agents themselves,[10] although of less-than-quantitative efficiency due to their ability to cyclopolymerize.[11] Reaction of the RHMA alcohol groups with difunctional epoxides[12] or with the azlactone group of a new functional vinyl monomer (to give an acrylamide and acrylate-containing dimer[13]) generated efficient difunctional cross-linking agents. Alternatively, polyesterification generated oligomers of glycolic acid containing randomly incorporated RHMA residues capable of serving as cross-linking sites.[14] We felt it desirable to extend these approaches to more controllable synthesis of new unsaturated polyesters of structure **3**.

The ether-forming dimerization of α-(hydroxymethyl)-acrylate groups was initially postulated to involve the transition state shown in Figure 1.[8] Subsequent mechanism studies using ^2H- and ^{13}C-labeled formaldehyde to generate the correspondingly labeled intermediate alcohols have not only substantiated this process but have also demonstrated additional and unexpected steps.[15] For the present discussion, the most important of these involves transetherification. That is, the initially formed ether linkage is susceptible to attack by another RHMA alcohol oxygen to give a new (but perhaps structurally identical) ether compound through displacement of an alcohol oxygen previously involved in the ether bond. The importance of this process will be discussed later in relation to product equilibration.

Two distinct steps exist in the formation of the desired acrylate oligomers. The first involves attack on the acrylate end groups of diacrylates such as that of 1,6-hexanediol. This DABCO-catalyzed insertion proceeds through a Michael-like addition-rearrangement-elimination reaction.[7] After formation and buildup of the hydroxymethyl groups, etherification takes place through a base-promoted attack on the β-carbon of the vinyl group of one of the substituted acrylates by the hydroxyl of another molecule.[8,15] A cyclic transition state is postulated involving concomitant ether bond formation and loss of water (see Figure 1). When carried out with equimolar amounts of formaldehyde and the diacrylate, the ether-forming reaction results in gradual chain extension through a step-growth mechanism to produce polymers of structure **3**.

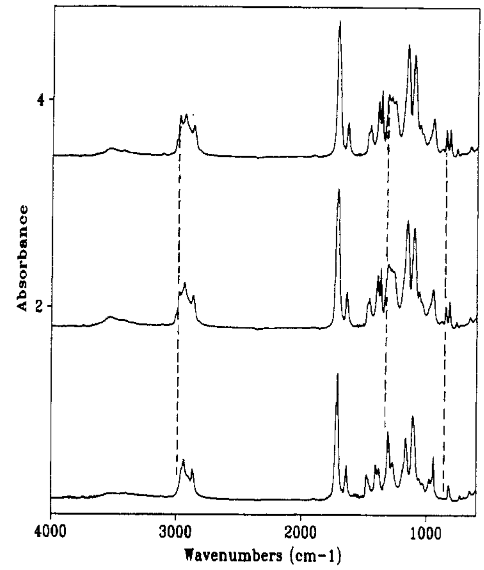

Figure 2. FTIR spectrum (KBr pellet) of a typical sample of polymer **3** (lower trace) and two *tert*-butyl acrylate terminated oligomers of decreasing molecular weight from middle to top traces.

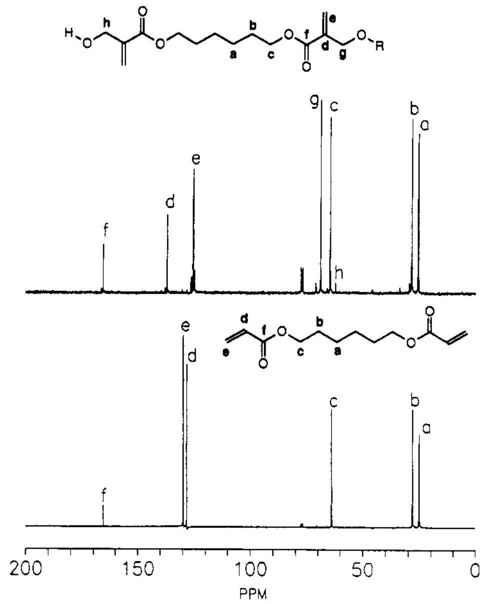

Figure 3. Solution ^{13}C NMR spectra with peak assignments of 1,6-hexanediol diacrylate (lower trace) and a typical sample of polymer **3** (upper trace) both taken in CDCl$_3$.

Product structure was confirmed by FTIR and ^{13}C NMR spectroscopy (Figures 2 and 3). The IR spectrum (lower trace, Figure 2) shows a broad OH peak at 3300 cm^{-1} for terminal alcohol groups resulting from incomplete conversion to ether linkages. Peaks for the internal acrylate carbonyls and vinylidine groups are clearly seen at 1710 and 1642 cm^{-1}. Peak assignments for ^{13}C spectra (Figure 3) of the starting material and obtained oligomer were made using previously characterized monomers, ether dimers, and polymers.[7-15] Comparison of the peak labeled h on the structure fragment in the spectrum (corresponding to hydroxymethyl end-groups) with the ester and ether methylenes c and g gives an estimate of the degree of polymerization (DP) for this product of 8–12. Small shoulders (barely visible in this spectrum) next to peaks e and f for the main repeat unit components correspond to the terminal alkene and ester groups, respectively, and are consistent with this estimate of the DP. Depending on reaction conditions such as temperature, time, concentration of catalyst, and whether or not the byproduct water is removed from the reaction, the average DP for materials prepared this way can vary over a wide range as dictated by a step-growth polymerization involving a slow and reversible coupling reaction between end groups. In fact, the DP was difficult to control by using this two-reactant system, and a method of controlling molecular weight (discussed below) was developed.

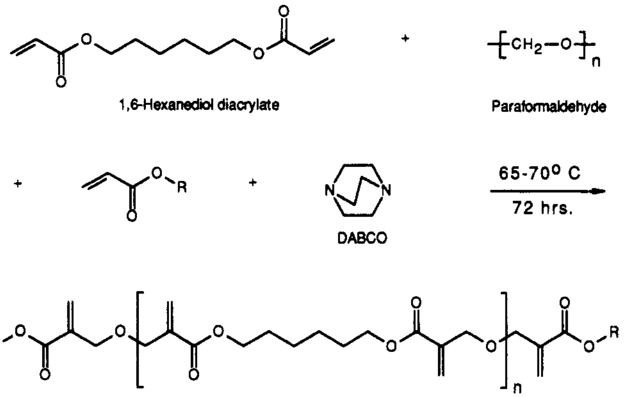

Figure 4. Overall process for oligomerization with end-capping.

The "cleanness" of the polymer-forming etherification was additionally compromised by acetal incorporation. That is, a competitive process occurs in which two alcohol groups react with formaldehyde and its oligomers to give one or more acetal segments in place of the more stable ether linkage.[8] The ^{13}C peaks for such acetals segments in place of the more stable ether linkage.[8] The ^{13}C peaks for such acetals are observed at ca. 95 ppm and are clearly absent here and in the compounds described below. This is due to the reversibility of the acetal-forming reaction and the greater stability of the ether group. That is, allowing the reaction to continue at elevated temperature eventually resulted in conversion of the acetal groups to ether linkages. At the same time, molecular weight should continue to increase for non-end-capped systems. Without added end-capper, however, and in the absence of water removal, an equilibrium molecular weight is apparently attained that depends on the thermodynamcis of the system. We have shown, in fact, that heating performed ether dimer in the presence of DABCO and added water leads to partial reversion to the RHMA alcohol; such reaction here would inherently limit molecular weight.

Bulk polymerizations were performed using this cross-linking agent (or an analogous material from a different batch) with methyl methacrylate and styrene. Although there were some problems with solubility, cross-linking was generally quite successful. During styrene polymerization, however, phase separation often occurred to give clear and cloudy layers, both of which were insoluble, indicating that cross-linking took place in both. With methyl methacrylate, no phase separation was apparent although cloudiness in the final rigid polymer was observed occassionally.

It was postulated that the problem with solubility and phase separation was due to the molecular weight of the cross-linking agent, and perhaps also to the presence of terminal alcohol groups. To controllably lower the molecular weight, ethyl acrylate or *tert*-butyl acrylate were added to the 1,6-hexanediol diacrylate to act as end-capping agents in the alcohol incorporation and etherification reaction (Figure 4). Assuming either comparable reactivity of the two types of acrylate esters or equilibration after ether formation, molecular weight should depend

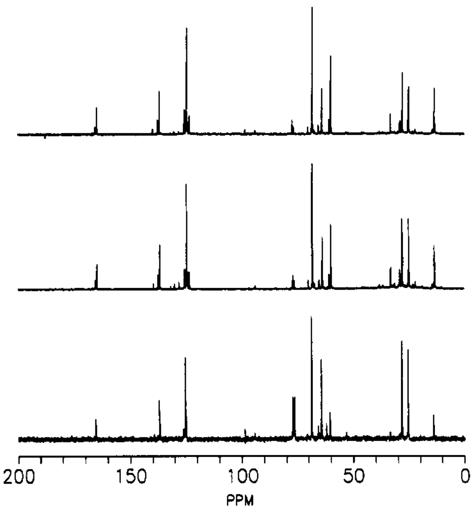

Figure 5. Solution ^{13}C spectra of three samples of ethyl acrylate terminated oligomers with decreasing molecular weight going from bottom to top.

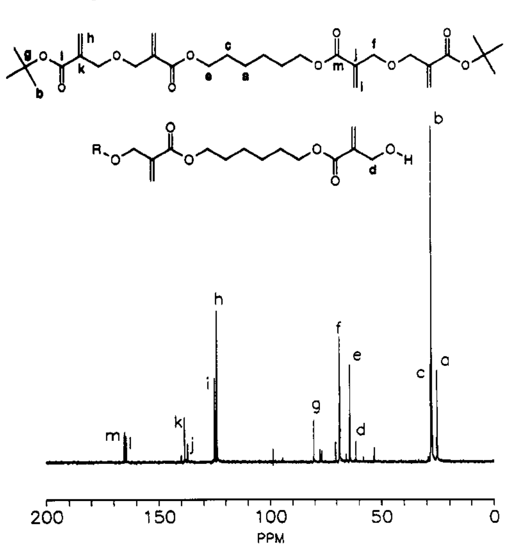

Figure 6. Solution ^{13}C spectrum with peak assignments of the lowest molecular weight species end-capped with *tert*-butyl acrylate.

upon the ratio of the two reagents and the amount of equilibrium water present. In addition, the oligomers formed should contain internal and terminal acrylates all linked through ether groups at their β-methylenes as indicated. FTIR and ^{13}C NMR confirmed the essential lack of terminal alcohol groups. Figure 2 includes the FTIR spectra of two oligmers containing increasing amounts of *tert*-butyl acrylate as end-capper along with the spectrum of the non-end-capped oligomer. Key differences are indicated by the dotted lines, which point out new peaks associated with the end-caps. These new peaks correspond to C–H, C–O, and C=C bond absorptions going from high to low wavenumber, respectively.

Figure 5 gives the ^{13}C spectra of three ethyl acrylate end-capped oligomers after purification with increasing ethyl acrylate ratio going from bottom to top. Comparison with the upper spectrum in Figure 3 allows ready identification of peaks associated with the end-group carbons. Most pronounced are the peaks at 14.0 and 60.5 ppm for the ester CH_3 and CH_2O carbons, respectively. The average DPs of the materials obtained (estimated from ^{13}C peak intensities) were consistent with the feed ratios.

These materials displayed excellent miscibility with both styrene and methyl methacrylate. Bulk thermal polymerization of reaction mixtures with ca. 5 wt % of the cross-linkers gave insoluble but swellable products with good clarity and toughness. Solid-state ^{13}C CP/MAS NMR spectra were obtained for these materials as well as the products containing the alcohol-terminal oligomers. Relative peak intensities for the former were consistent with feed compositions, although since essentially quantitative conversion occurred, all monomer and cross-linker should be incorporated. The two phases for the styrene system showed different oligoacrylate contents with one being nearly free of any cross-linker; both were insoluble and did show peaks consistent with incorporation of the acrylate oligomers.

The end-capping reaction with *tert*-butyl acrylate was examined for two reasons. First, the bulky ester group should give a lower bound measure of steric inhibition to the oligomer termination reaction which involves reaction of the intermediate *tert*-butyl α-(hydroxymethyl)acrylate (TBHMA) with itself and the terminal α-(hydroxymethyl)-acrylate group generated during oligomerization. Second, the *tert*-butyl ester group is easily converted to the corresponding free acid thermally or by reaction with trifluoroacetic acid, providing a pathway to a family of oligomers that should be water soluble or water dispersible. The spectrum in Figure 6 corresponds to a product obtained from a mixture containing excess *tert*-butyl acrylate. This was one of several attempts to generate very low molecular weight oligomers even to the point of stopping the oligomerization reaction altogether to give the structure shown. In fact, this effort was successful. Peak assignments indicated were made based on analogous spectra shown in Figures 3 and 5 and on the spectra of TBHMA and its isolated and purified dimer. The ratio of peaks shown, along with integration values from the ^1H spectrum, confirmed the product as mainly a mixture of the upper structure drawn in Figure 6 and the TBHMA ether dimer. This finding indicates that even if oligomerization of the 1,6-hexanediol diacrylate did take place, thermal equilibration during synthesis and partial distillation (to remove byproduct water, TBHMA, and some TBHMA dimer) gave the end-capped starting material as a major product. Incidentally, the peak marked d and the small peaks just downfield of e, f, and k correspond to terminal α-hydroxymethylacrylate groups and adjacent carbons as indicated in the lower structure drawn in Figure 6. With lower ratios of *tert*-butyl acrylate to HDDA, increasing chain length of the end-capped oligomers was observed. After workup involving removal of any byproducts, catalyst, and most end-capper dimer, the solution ^{13}C NMR spectra show peaks consistent with the expected structures.

Removal of the *tert*-butyl ester group was facile. Simply stirring with trifluoroacetic acid (TFA) in chloroform followed by rotary evaporation gave complete deprotection. Figure 7 gives the 20–85 ppm region of spectra of a *tert*-butyl acrylate end-capped oligomer and of its free-acid derivative after reaction with TFA. Notably absent are the methyl and quaternary carbons of the *tert*-butyl moiety at 27.9 and 80.7 ppm, respectively. Peaks for the acid end groups and nearby esters appear at 171.2 and 168.0 ppm (not shown), significantly downfield from their ester positions at ca. 165 ppm. The particular sample characterized in Figure 7 contains ca. 50% ether dimer of TBHMA, which was also deprotected and contributes to peak complexity in the ester and ether α-carbon and olefinic regions at 65–70 and 125–140 ppm, respectively. While we have not yet examined use of this material as a cross-linker for water-dispersible monomers, previous success with the free acid of the ether of α-(hydroxymethyl)acrylate supports its potential applicability.[10]

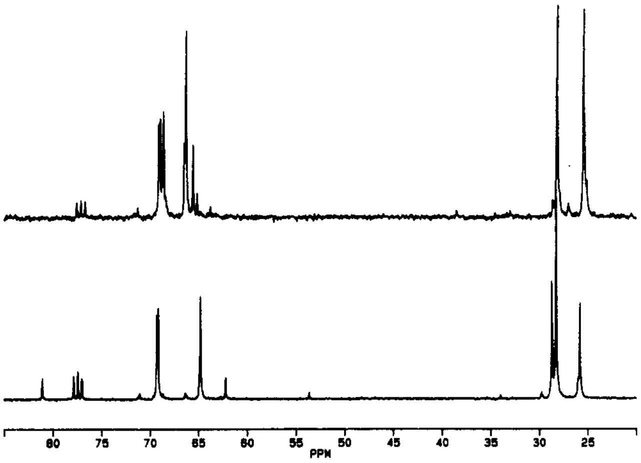

Figure 7. The 20–85 ppm region of the solution ^{13}C spectra of *tert*-butyl acrylate end-capped oligomer (lower trace) and its deprotected free acid (upper trace).

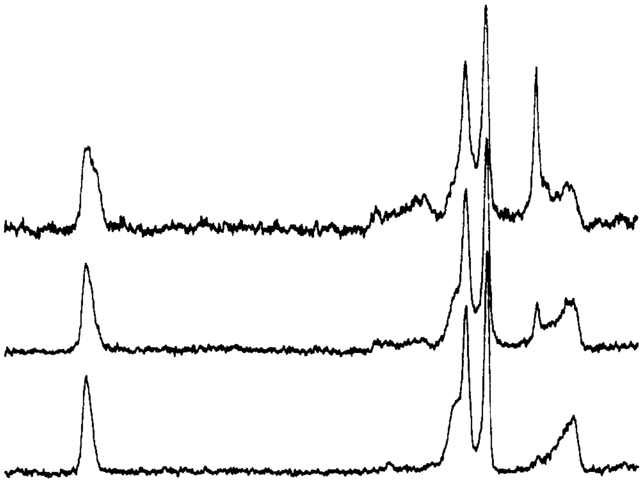

Figure 8. Solid-state ^{13}C spectra of three samples of poly(methyl methacrylate) cross-linked with 5, 20, and 50% of the *tert*-butyl acrylate end-capped oligomer containing ca. 2–3 HDDA repeat units.

Various members of the series of TBHMA-terminal oligomers were examined as cross-linking agents at up to 50 wt % with methyl methacrylate and styrene in photoinitiated polymerizations. While photocure of the neat oligomers occurred very rapidly, these highly cross-linked products were brittle. In contrast, copolymerization gave products that were clear to hazy, but that possessed excellent toughness and resistance to solvent swelling and breakup. Qualitative evaluation of rate of cure indicated that the $^1/_4$-in.-thick samples containing 50% or more of the oligomers gelled rapidly and were very hard within 10 min. Lower concentrations gave lower cure rates with the 5% compositions requiring ca. 60 min for complete polymerization under our conditions. Qualitative evaluation of toughness indicated that at higher cross-linker concentrations, especially greater than 20%, samples became brittle and failed more easily than those with lower concentrations. Solid-state ^{13}C NMR confirmed complete consumption of the vinyl groups in all samples as illustrated by the spectra in Figure 8. Incorporation of the *tert*-butyl acrylate end-capped oligomer is confirmed by the sharp methyl peak at ca. 30 ppm, broad peaks for ether and ester carbons α to oxygen at 65–85 ppm, and a carbonyl shoulder on the upfield side of the PMMA carbonyl at 178 ppm.

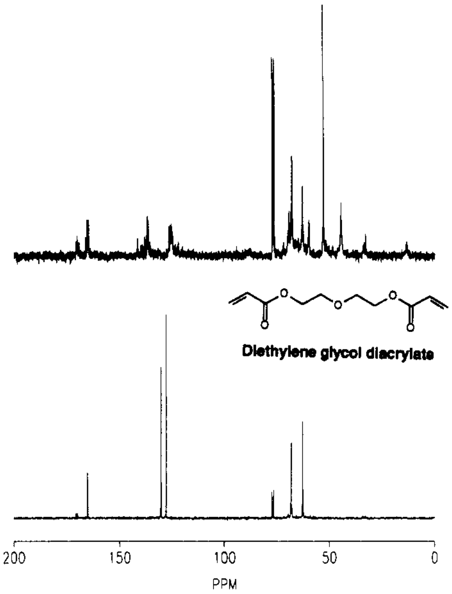

Figure 9. Solution ^{13}C spectra of diethylene glycol diacrylate (lower trace) and oligomer from a 5:1 ratio of diacrylate to ethyl acrylate (upper trace).

Finally, the oligomerization process was extended to potentially water-soluble derivatives of oligo(oxyethylene) diacrylates. Figure 9 gives the ^{13}C solution spectra of the diethylene glycol diacrylate and a chain-extended oligomer obtained with ca. 20 wt % added ethyl acrylate. Similar spectra wre obtained for the corresponding tetraethylene glycol compounds. In both cases, use of ethyl acrylate as end-capper at this relatively low concentration led to much higher DP oligomers compared to those obtained with HDDA described above. While these materials should function as cross-linkers for both organic and water-soluble monomers, we have not examined their use in such applications.

It should be mentioned that others have shown that additional diacrylates undergo methylene ether chain extension readily.[6] In addition to observations similar to ours[5] regarding non-end-capped oligomerization of HDDA, diacrylates of a partially fluorinated diol and bisphenol-A bis(hydroxyethyl) ether were also reported to undergo facile conversion to reactive oligomers with paraformaldehyde and DABCO. However, the fluorinated species gave an unexpected 1,4-diene repeat unit in a 2:1 ratio with the $-CH_2OCH_2-$ containing 1,6-diene groups. Apparently, a carbon-centered anion resulting from Michael addition of DABCO to one of the acrylate end groups attacks a terminal $-CH_2OH$ with subsequent loss of H_2O and DABCO to give a single CH_2 unit between α-carbons of two acrylate units.[15]

In summary, this procedure provides a practical method of synthesis and isolation of new oligomeric materials that can function as cross-linking agents. Rapid chain extension is coupled with straightforward workup to remove the DABCO and unreacted acrylate monomer. The former involves extraction or filtration through activated acidic alumina, and the latter simply involves rotary evaporation. While some unreacted terminal hydroxymethyl groups remain (if water is not removed during synthesis) along with small amounts of the dimer ether of the acrylate end-capper, these generally have little or no effect on oligomer performance as cross-linkers. It should be mentioned, however, that for both the ethyl and *tert*-butyl acrylate terminated oligomers, increasing chain length causes an increase in melting point from below to above room temperature. That is, while compounds containing 2–4 HDDA repeat units are liquids, those with more than ca. 5 are solids. In any event, it is clear that this method for generating reactive acrylate-containing oligomers is general and, when coupled with the end-capping procedure described here, provides an excellent method for controlling both the oligomer molecular weight and the terminal functionality of the end-capping groups.

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Registry No. 3 (copolymer), 129573-59-7; 3 (SRU), 132622-20-9; (diethylene glycol diacrylate)(ethyl acrylate) (copolymer), 25119-91-9.