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Polymerization of 2-hydroxyethyl acrylate and methacrylate *via* Michael-type addition

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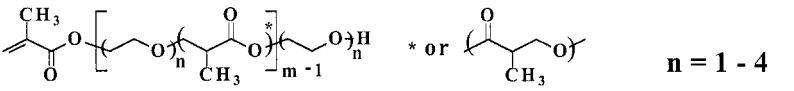
Summary

2-Hydroxyethyl acrylate was polymerized by use of few basic and/or nucleophilic initiators. The reactions proceeded *via* Michael-type addition of hydroxyl groups to carbon-carbon double bonds. The resulted polymers have an ether-ester chain structure and M_n values in order of up to 9000. The results were compared with those obtained previously for 2-hydroxyethyl methacrylate, where just oligomers having M_n of *ca* 1000 had been achieved.

Introduction

Recently we have reported on oligomerization of monomethacrylates of oligoethylene glycols, including 2-hydroxyethyl methacrylate (HEMA), proceeding *via* Michael-type addition of hydroxyl groups to methacrylate carbon-carbon double bonds. This slow, irreversible reaction had been acompanying fast, reversible disproportionation of monomethacrylates to dimethacrylates and corresponding glycols. Oligo(ether-ester)s formed, shown in Scheme 1, have molecular weight in order of one thousand, as it was stated by ^{1}H NMR, GPC and ESI-MS analyses. Attempts to attain higher molecular weight products did not succeed since both temperature and prolonged reaction time caused gelation of the system [1].



Scheme 1. Structure of the oligo(ether-ester)s formed by Michael-type addition of monomethacrylates of oligoethylene glycols (for HEMA n=1)

Acrylate monomers are known to be much more susceptible to Michael addition when compared with methacrylates, which is due to the difference in charge density distribution [2]. Oligomerization of hydroxyacrylates had been reported several years ago in the patent literature [3]. Recently, dihydroxyacrylates were polymerized according to that mechanism to yield hyperbranched polymeric systems [4, 5]. The difference in reactivities of acrylate and methacrylate groups was exploited to

synthesize novel dental methacrylate resin *via* selective Michael addition of alkoxysilane-amines to the acrylate double bond in the presence of the methacrylate one [6]. It might be interesting therefore, to compare the behaviour of an acrylate monomer with a corresponding methacrylate one in a reaction regime providing oligomerization of the latter. Here, we present results on comparison of polymerization of HEMA and 2-hydroxyethyl acrylate (HEA) involving Michael-type addition mechanism.

Experimental

Materials

HEMA (Sigma) and HEA (Aldrich) were dried over anhydrous $MgSO_4$. NaH (sodium hydride, Aldrich – suspension in mineral oil) was washed several times with dry tetrahydrofurane and dried under reduced pressure. PPh_3 (triphenylphosphine), *t*-BuOK (potassium *tert*-butoxide) and PTZ (phenothiazine) were supplied by Aldrich whereas K_2CO_3 and KOH by POCh; all used as received. Solvents and other auxiliary chemicals were of commercial grade.

Polymerization

The mixtures of the monomer and the initiator in 20:1 molar ratio were stirred magnetically under dry nitrogen. PTZ (0.15 % by weight) was added to prevent free-radical polymerization of carbon-carbon double bonds. The temperature was kept at the "optimal" level, i.e. in the range of 80-150°C, as it was established previously [1] for each the initiator in the case of polymerization of HEMA, except for when using *t*-BuOK and NaH to polymerize HEA, where room temperature has been employed. After 2 hrs the reaction mixtures were examined by ^{1}H NMR, except for NaH/HEA one where gelation occurred very fast and the analyses had to be performed after 15 min. Those exhibiting highest conversion of double bonds were neutralized by 1% HCl and extracted by $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$ and filtered, afterthat the chloroform was removed with an rotary evaporator. The final products were analyzed by NMR and GPC.

Measurements

^{1}H NMR spectra were recorded with the aid of UNITY/*INOVA* 300 MHz spectrometer (Varian) using $CDCl_3$ as a solvent and TMS as an internal reference.
GPC analyses were performed in THF (1mL/min) at 30°C using Knauer chromatograph with RI detector and 2xPlgel Mixed-C plus 1xPlgel 100 Å column set, calibrated with polystyrene standards.

Results and discussion

Since HEMA, its disproportionation products and resulted oligomers have relatively readable ^{1}H NMR spectra, we were able to monitor course of the reactions and to characterize the final products using this technique [1]. The spectra of HEA reactions mixtures are more complex. However some signals could be selected to obtain quantitative data. A typical spectrum recorded at an intermediate conversion level is shown in Figure 1.

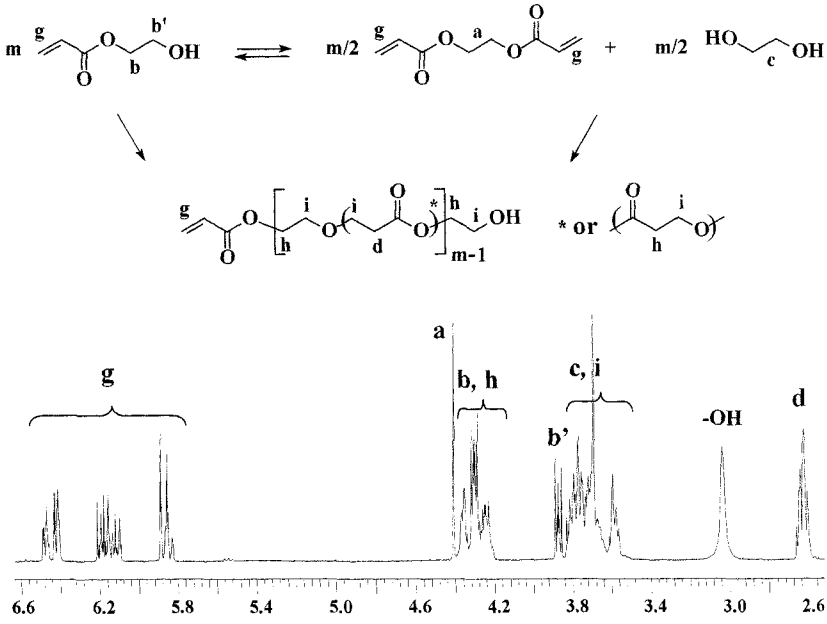


Figure 1. ^{1}H NMR spectrum of HEA polymerization reaction mixture

The disproportionation of HEA yields ethylene glycol and its diacrylate in an equimolar ratio. The oxyethylene protons of the latter, H_a, exhibit a singlet at δ=4.41 ppm, separated enough to be integrated and thus to determine conversion (α_{disp}) in that reaction path:

$$\alpha_{disp} = \frac{I_a}{2I_0} \tag{1}$$

where I_0 denotes initial signals intensity related to one proton:

$$I_0 = \frac{I_d}{2} + \frac{I_g}{3} \tag{2}$$

The addition of the hydroxyl proton to the acrylate C=C double bond yields appearance of a triplet of the H_d protons at δ=2.63 ppm. A half of the intensity of this signal corresponds to the decrease of the intensity of the signals of the vinylic protons (multiplets at δ=5.8-6.5 ppm). Thus, similarly as we did for HEMA [1], we can determine the fraction of C=C bonds which underwent Michael addition (F_{add}):

$$F_{add} = \frac{I_d}{2I_0} \tag{3}$$

Assume the disproportionation and the polymerization *via* Michael-type addition are the only reactions that proceed in the system, the total conversion of HEA (α_{tot}) can be expressed as:

$$\alpha_{tot} = \alpha_{disp} + \alpha_{add} \quad (4)$$

where α_{add} denotes conversion in Michael-type addition path.

On the other hand, total conversion of HEA can be estimated from the decrease of the intensity of its oxyethylene protons:

$$\alpha_{tot} = 1 - \frac{I_b}{2I_0} \quad (5)$$

The ^{1}H NMR based quantitative results on polymerization of HEA are compared in Table 1 with those obtained previously [1] for HEMA. As it is seen, even the species being quite inefficient in initiating polymerization of HEMA, i.e. KOH and PPh_3, catalyze conversion of double bonds (and thus initiate polymerization) of HEA in a considerable extent. The most efficient initiators for HEMA, i.e. *t*-BuOK and NaH, are also very active towards HEA, even at room temperature.

Table 1. ^{1}H NMR based quantitative data after 2 hrs for HEA and HEMA disproportionation/polymerization reactions

Initiator	HEMA[a]				HEA			
	Temp. [°C]	α_{disp}	α_{tot}	F_{add}	Temp. [°C]	α_{disp}	α_{tot}	F_{add}
K_2CO_3	150	0.36	0.65	0.15	150	0.07	0.91	0.61
KOH	150	0.42	0.45	0.01	150	0.13	0.82	0.48
t-BuOK	100	0.20	0.78	0.35	25	< 0.01	≈ 1	0.94
NaH	80	0.20	0.80	0.37	25	< 0.01	≈ 1	0.98[b]
PPh_3	85	0.33	0.33	0.00	85	0.09	0.85	0.74

[a] results presented recently [1]
[b] after 15 min

It should be kept in mind that the products of mono(meth)acrylate disproportionation reaction, i.e. di(meth)acrylate and corresponding glycol, take part in polymerization *via* Michael-type addition as well. Thus, values of α_{disp} measured are in a way artificial ones, since they inform on an actual fraction of disproportionation products which have not polymerized as yet.

The ^{1}H NMR data enables estimation of number average degree of polymerization of the resulted polymers (*m* in Scheme 1 and Figure 1) by simple relating conversion of the monomer in this reaction path (α_{add}) to the F_{add} value:

$$\alpha_{add} = F_{add} \frac{m}{m-1} \quad (6)$$

However, in the case of the reactions initiated by *t*-BuOK and NaH the spectra of the final products exhibited presence of neither HEA nor corresponding diacrylate. Thus, it can be assumed that $\alpha_{tot} \approx \alpha_{add} \approx 1$ and in consequence Equation 6 may be simplified to the following one:

$$F_{add} = \frac{m-1}{m} \quad (7)$$

The values of number average molecular weight (M_n) estimated for the above crude final products by use of Equation 7 amount to *ca* 2100 and 6300 for *t*-BuOK and NaH respectively. The same materials, when examined by GPC after purification (see experimental part), were found to have values of M_n in order of 8000 to 9000 (M_w in order of 20000 to 25000). Exemplary chromatograms are shown in Figure 2.

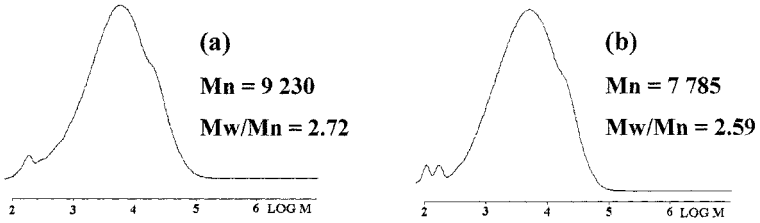


Figure 2. GPC traces of the HEA polymers obtained with (a) NaH, (b) *t*-BuOK

In some of the experiments we have observed appearance of two new signals (δ=5.65 and δ=6.22 ppm) in the vinylic region of ^{1}H NMR spectra, especially in the final stage of the reaction (Figure 3). This is consistent with the observation of Kadokawa *et al* [4, 5] who had asigned them to the side reaction yielding formation of the α-substituted acrylate group. The authors had observed that when using PPh_3 as an initiator in the polymerization of 2,2-bis(hydroxymethyl)propyl acrylate whereas had not when initiating with NaH. In our experiments, the signals appeared when initiating by *t*-BuOK, NaH and PPh_3 whereas did not when using K_2CO_3 and KOH. According to Kadokawa, the side reaction involves elimination of formaldehyde which reacts with carbanion formed at the α position. In our opinion, formation of formaldehyde in HEA polymerization system would be rather inexplicable and we think that α-carbanion simply reacts with either terminal acrylate carbon or carbonyl one, as it is shown in Scheme 3. Since high-field side H_j signal is a double one, one may expect at least two of such structures to be formed. The ratio of the acrylate groups to the α-substituted ones was found to be about 2:1, as it was estimated based on the intensities of the ^{1}H NMR signals.

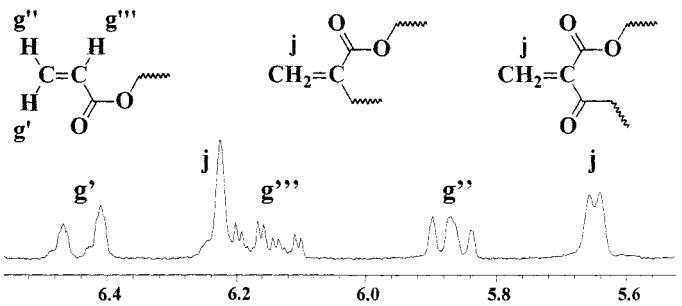
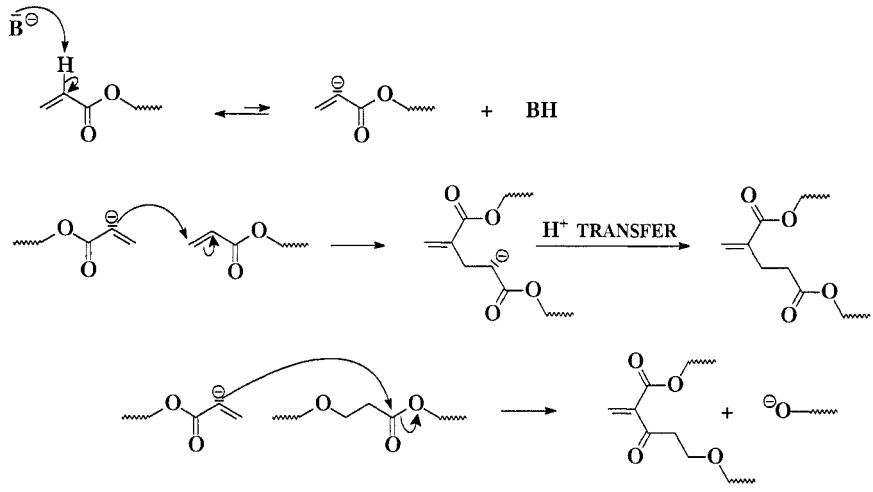


Figure 3. A fragment of ^{1}H NMR spectrum of HEA polymerization mixture presenting the signals of the α-substituted acrylate group formed



Scheme 2. Possible mechanism of the formation of the α-substituted acrylate group during polymerization of HEA

Conclusions

In the presence of basic and/or nucleophilic initiators, HEA polymerizes according to Michael-type addition mechanism. The process proceeds very readily when compared with analogous experiments performed on HEMA. The poly(ether-ester)s formed have M_n values amounting up to about 9000 whereas just oligomers of HEMA had been obtained. Sodium hydride and potassium *t*-butoxide appeared to be the most efficient initiators for both HEA and HEMA polymerization.

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