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Michael addition polymers from 1,4 and 1,3 benzenedimethanol diacetoacetates and tripropylene glycol diacrylate

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Summary

The Michael reaction was used to synthesize polymers from diacetoacetate esters and the diacrylate of tripropylene glycol. The reaction took place readily, although slowly, at room temperature using 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) as the catalyst. The polymers produced had quite high molecular weights (M_w) in some cases, but the molecular weight distributions were quite broad, particularly in the initial polymer formed. The narrowing of the molecular weight distribution with time can be explained by consideration of the mechanism of the Michael reaction.

Introduction

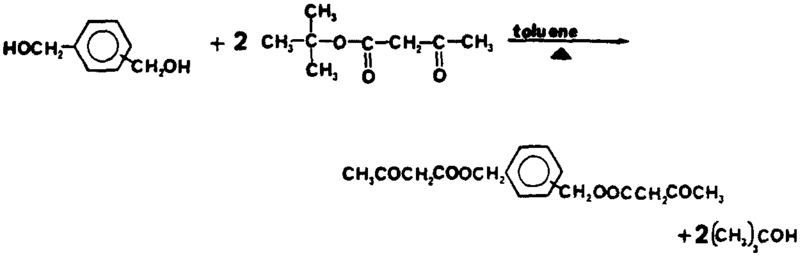
Acetoacetylation of hydroxy groups as a means of reducing polymer solution viscosity while maintaining reactivity was demonstrated some time ago (1,2). However, until recently there was no safe, cost effective way of synthesizing acetoacetates in high yields (3-5). The introduction, by Eastman Chemical Co., of t-butyl acetoacetate (5,6) makes possible the safe, facile and economical synthesis of acetoacetate esters in high yields. We therefore undertook the synthesis of several such esters in order to study their polymerization behavior. In particular we wanted to take advantage of the active methylene functionality of acetoacetate esters. Therefore, we chose Michael addition as a polymer-forming reaction because the well-know acidity of the methylene protons of acetoacetate esters insures their ready participation in base catalyzed reactions such as the Michael reaction.

Experimental

All solvents and reagents used in this study were reagent grade materials and were used without further purification. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. ^{1}H-Nmr spectra were obtained at ambient temperature using a Perkin-Elmer R-32 spectrometer operating at 90 MHz in the CW mode. Glass transition temperature measurements were made, with a DuPont 2100 Thermal Analyzer, under nitrogen at a scan rate of 10°C/min. Molecular weight measurements were made with a Waters 150/ALC GPC equipped with 1 x 10^6, 1 x 10^5, 1 x 10^4, 1 x 10^3, 500 and 100Å ultrastyragel columns. Tetrahydrofuran was used as the eluent.

Acetoacetate Ester Synthesis

The 1,4 and 1,3 benzenedimethanol acetoacetate esters (1,4 BDDA and 1,3 BDDA) were synthesized as shown in Scheme I.



Scheme I

Thirty grams of the diol (1,4 or 1,3) and 68.6 grams of t-butyl acetoacetate were charged into a flask containing 180 ml of toluene and equipped with a mechanical stirrer, reflux condenser, thermometer and Dean-Stark trap. The reaction mixture was heated to 105°C at which point the rapid evolution t-butanol commences, with the theoretical amount being collected in 20-40 min. The reaction mixture was allowed to cool, the toluene was removed on a rotovap at 40-50°C. In the case of the 1,4 isomer the residue was a viscous yellow-orange oil that crystallized after standing at room temperature for 1h. Purification was effected by recrystallization from hexane/acetone/diethyl ether 7/2/1. The yield of bright white crystals was 81.2%, m.p. = 65°C (sharp). ^{1}H-Nmr, $CDCl_3$; δ 2.25 (s.s., 6H); δ 3.52 (s.s., 4H); δ 5.10 (s.s., 4H); δ 7.28 (s.s., 4H).

Polymer Synthesis

Polymers were synthesized by charging 5.00g (0.016 mol) of 1,4 or 1,3 BDDA into a 125 ml Erhlenmeyer flask equipped with a magnetic stirrer. Solvent (45 ml) was then added followed by 4.91g of 95% tripropylene glycol diacrylate (TPDA). The BDU was then added (0.2g, 0.0013 mol) and the flask was tightly stoppered. The reaction mixture immediately became light yellow in color. The reaction mixture was stirred at ambient temperature for 120h during which time the color changed to dark yellow-orange. Samples (2 ml) were withdrawn at intervals and polymer was precipitated by addition to excess cold diethyl ether. Purification was effected by dissolving the polymers in $CHCl_3$ and precipitating into a 7-8 fold excess of cold diethyl ether. After 120h, the entire reaction mixture was poured into excess cold diethyl ether. The polymer that precipitated was purified as described. The polymers were dried in vacuo at 30°C for 72h, then weighed to determine conversion. The weight of all polymer observed, that from samples withdrawn as well as the polymer obtained after 120h, was added together to determine the conversion from a single polymerization.

The amount of TPDA added corresponds to 0.0155 mole of active acrylate, a less than stoichometric amount. In two experiments the amount of TPDA was adjusted to provide the stoichometric amount of double bond functionality, in both of these experiments the reaction mixture gelled in $\sim$8h. Therefore, in all subsequent experiments, a slight excess of diacetoacetate ester was used. The purity of the TPDA was established by GC analysis, the major impurities are the monoacrylate (4.1-4.4 wt %) and methyl acrylate (0.6-0.9 wt %).

Results and Discussion

All polymer obtained, including any samples withdrawn, was analyzed by ^{1}H-nmr and GPC. The results and spectra obtained are given in Table I and Figure 1 respectively.

TABLE I

Polymerization Conditions, Conversions and Molecular Weights

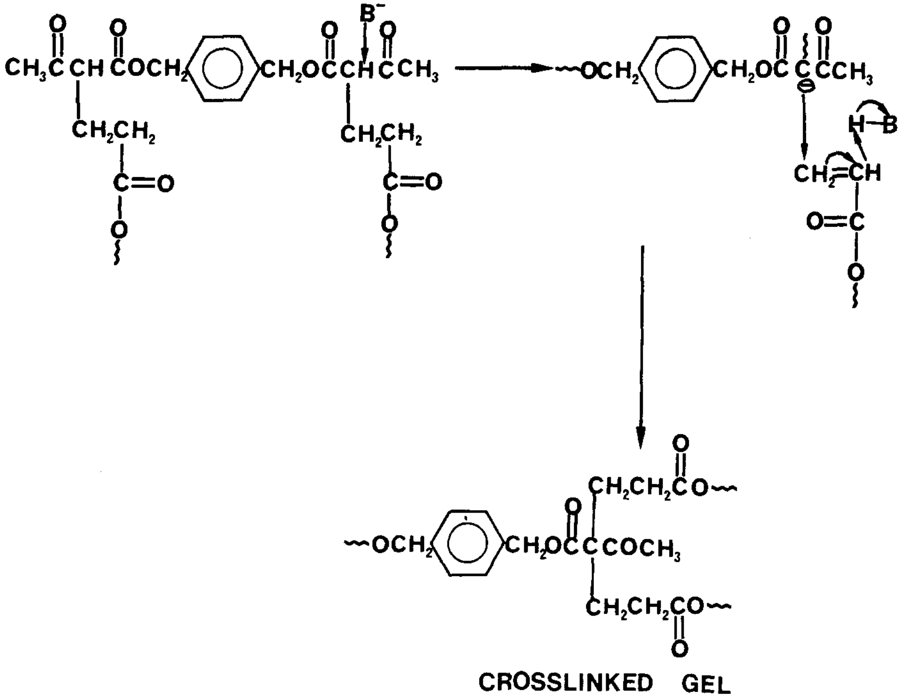
Polymer	Solvent	Reaction Time (h)[a]	Conver. (wt %)	M_n	M_w	M_w/M_n
1,4 BDDA-TPDA	2-butanone	24	-	7300	74300	10.18
1,4 BDDA-TPDA	2-butanone	96	-	2500	18200	7.28
1,4 BDDA-TPDA	2-butanone	120	80.3	3000	21300	7.10
1,4 BDDA-TPDA	2-butanone/ n-butanol[b]	36	-	8200	64000	7.80
1,4 BDDA-TPDA	2-butanone/ n-butanol	120	40.7	8100	43000	5.27
1,3 BDDA-TPDA	2-butanone	48	-	9200	436600	47.46
1,3 BDDA-TPDA	2-butanone	72	-	9000	121000	13.44
1,3 BDDA-TPDA	2-butanone	120	71.0	5300	35000	6.60

a. Reaction times other than 120h indicate that these were samples withdrawn from the reaction mixture.

b. 6/1 v/v mixture of butanone/butanol.

The polymers have very broad molecular weight distributions which narrow considerably with time. The broadness of the molecular weight distribution is understandable, considering that the reactive groups are not stoichometrically balanced and conversions are considerably less than 100% (7). The narrowing of the distribution with time reflects the reversible nature of the Michael reaction particularly in the presence of catalysts (8,9). What we believe is happening is that i.e. a larger number of shorter chains are being produced, thus there is a narrowing of the molecular weight distribution. Because no further narrowing occurs after 120h, this is approximately the time taken to achieve this equilibrium.

As previously stated, stoichometric amounts of reactive groups leads to gelation. A possible reason for this occurance is the acidity of the second hydrogen of the active methylene group of the acetoacetates (8,9). This acidity would allow the methylene group to react twice with electron poor double bonds as shown in Scheme 2.



Scheme 2

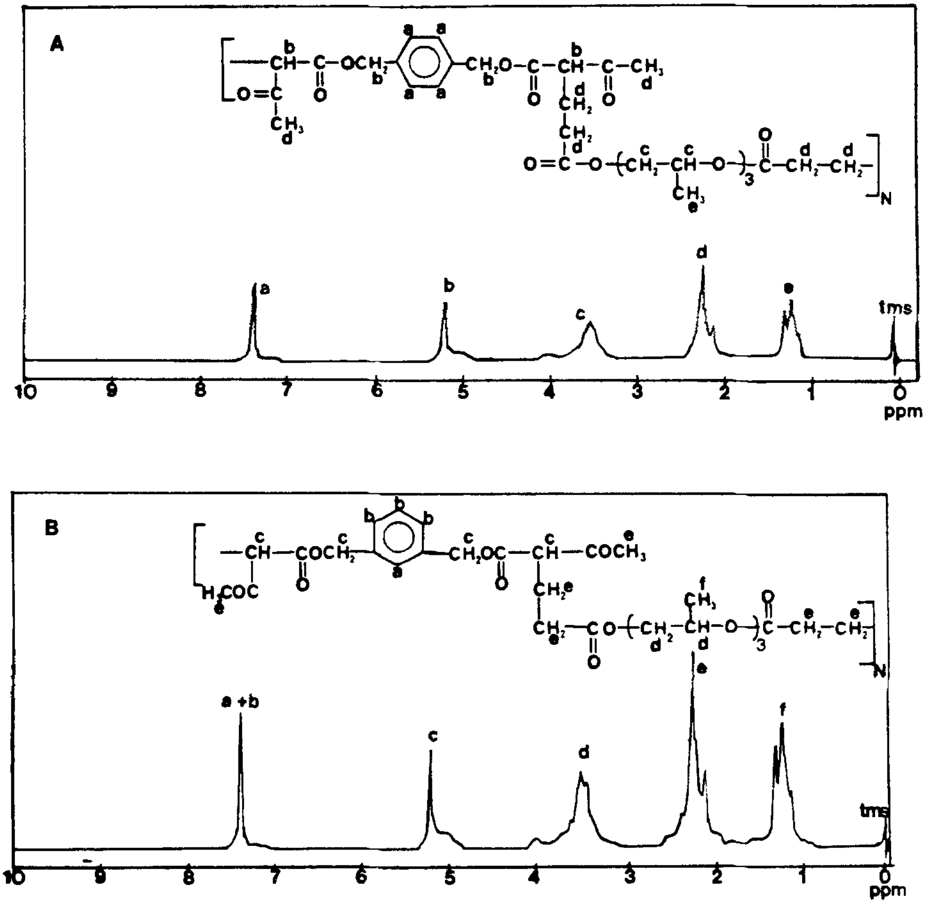


Figure 1: ^{1}H-Nmr spectra of the copolymers of: A) 1,4 BDDA and TPDA (120h) and B) 1,3 BDDA and TPDA (120h).

Due to steric hinderance this reaction would be slow, but a stoichometric amount of double bonds could eventually cause gelation of the reaction mixture through this type of reaction.

^{1}H-Nmr (Figure 1) confirms that the polymers have the expected structure (assignments made in the Figure). The spectra shown are for the 120h polymers, but the spectra for samples obtained at other times are not significantly different than these. The glass transition temperatures obtained for the 120h polymers are given in Table II.

TABLE II

Glass Transition Temperatures

Polymer	Pzn Solvent	Tg ^{o}C
1,4 BDDA-TPDA	2-butanone	$-13,4^{o} \pm 2^{o}$
1,3 BDDA-TPDA	2-butanone	$-10.8^{o} \pm 2^{o}$

The order of the Tg's is unexpected, i.e. one would predict polymers based on the 1,4 isomer to have higher Tg's. However, the molecular weight of the 1,3 polymer is higher and the molecular weight distribution is narrower, which could account for the apparently higher Tg of the 1,3 BDDA-TPDA copolymer.

Conclusions

Polymers based on the diacetoacetate esters of 1,3 and 1,4 benzenedimethanol have been synthesized via a Michael addition reaction with TPDA. While the polymers have broad molecular weight distributions, the molecular weights (M_W) are not low, although because of the high molecular weight of the repeat unit the average DP is not that large. However, the DP is sufficient for some very high molecular weight species to be produced. The polymers were found to have the structures expected via ^{1}H-nmr. A possible mechanism for the gelation observed at stoichometric ratios of reactants was proposed, however, more work will be necessary before this mechanism can be accepted as fact.

References

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