Polymer Bulletin 26, 481–485 (1991)

Polymer Bulletin

Michael addition polymers from bisacetoacetates

II. 2,2-dimethyl-1,3-bis(acetoacetyl)-propanediol and *N,N'*-bis(acetoacetyl)-1,4-piperazine

David L. Trumbo

The Glidden Company, 16651 Sprague Rd., Strongsville, OH 44136, USA

Summary

The Michael reaction was used to synthesize polymers from bisacetoacetyl esters and amides and a diacrylate. The reaction occurred readily at room temperature yielding semi-solid polymers with broad molecular weight distributions which narrowed as the reaction progressed. The polymers based on the amide had lower molecular weights than those based on the ester.

Introduction

In a previous communication (1) we showed the feasibility of using the Michael addition reaction to form polymers from bisacetoacetyl compounds and a diacrylate. Specifically, bisacetoacetates based on 1,3 and 1,4-benzene-dimethanol were used with tripropylene glycol diacrylate as the diacrylate comonomer. We have now extended this reaction to an aliphatic bisacetoacetate ester and a bis(acetoacetyl) amide (2). This paper is a preliminary report of our results.

Experimental

The t-butyl acetoacetate was supplied by the Eastman Chemical Co. and was used as received (98% purity). All other solvents and chemicals were reagent grade and were used without further purification. ^{1}H-Nmr spectra were recorded at ambient tempeature on $CDCl_3$ or d_6-DMSO solutions using a 90 MHz Perkin-Elmer R-32 spectrometer operating in the CW mode. Molecular weight determinations were made with a Waters 150/ALC GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100 A ultrastyragel columns. Numerical values for the molecular weight were obtained by comparison to a polystyrene calibration curve. Glass transition temperature measurements were performed with a DuPont 2100 Thermal Analyzer under nitrogen with a scan rate of 15^oC/min. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected.

Acetoacetate Ester Synthesis

The ester was synthesized by charging 1 mole of 2,2-dimethyl-1,3-propanediol (neopentyl glycol, NPG) into a 1l flask containing 650 ml of toluene, and equipped with a mechanical stirrer, thermometer and a Dean-Stark trap. Two moles of t-butyl acetoacetate, (t-BAA) were added and stirring and heating was begun. The reaction commences, as noted by the rapid evolution of t-butyl alcohol, when the pot temperature reaches 95°C. The theoretical amount of t-butanol is collected in 0.5h, but heating was continued for an extra 0.5h in order to insure complete reaction. The reaction mixture is allowed to cool to room temperature and the toluene was removed under reduced pressure. The residual orange-yellow oil was purified by boiling with activated charcoal in methyl ethyl ketone, followed by column chromatography on silica gel using methyl ethyl ketone as the eluent. After removal of the solvent the residual material is a very light yellow mobile oil (3). ^{1}H-Nmr $CDCl_3$; δ 0.95 (s.s., 6H); δ 2.20 (s.s., 6H); δ 3.50 (s.s., 4H); δ 3.90 (s.s., 4H). Yield = 92.8%.

N,N'-Bis(acetoacetyl)-1,4-Piperazine

This compound was synthesized via the same procedure detailed above (4). The proportions of reagents used were: piperazine = 0.58 mol., t-BAA = 1.16 mol., toluene = 360 ml. The reaction proceeded as above, with the total reaction time being 1h. The toluene was removed under reduced pressure, leaving a very viscous orange oil, which on standing overnight at 0°C, crystallized to a mass of off-white crystals. Purification was effected by dissolving the crystals in acetone, boiling this solution with activated charcoal, filtering, cooling the solution to room temperature and adding ether until a haziness was observed. This solution is then chilled overnight at 0°C, after which a large quantity of white crystals formed. The crystals were isolated by filtration and washed with cold ether. After 48h drying in vacuo the crystals were weighed to determine the yield (86%). The m.p. = 111-112°C. ^{1}H-Nmr, d_6-DMSO; δ 2.15 (s.s., 6H); δ 3.20-3.55 (m., 8H); δ 3.65 (s.s., 4H).

Polymer Synthesis

Polymers were synthesized by charging 5.00g of the bis(acetoacetyl) compound into a 125 ml Erhlenmeyer flask equipped with a magnetic stirrer. Solvent (45 ml) was then added followed by the tripropylene glycol diacrylate (5.52g for the NPG ester, 5.91g for the amide). Stirring was started and the catalyst, 1,8-diaza-bicyclo [5.4.0] undec-7-ene (DBU), 0.21g was then added. The flask was tightly stoppered and the reaction was allowed to proceed at room temperature for 120h. Samples were periodically withdrawn, the polymer precipitated, purified and analyzed for molecular weight and molecular weight distribution. After 120h the polymerization was terminated by pouring the contents of the flask into an 8-fold excess of cold ether. The polymer was washed with several portions of ether, then purified by dissolving in $CHCl_3$ and reprecipitating into an 8-fold excess of cold ether. All samples were purified in this manner. The polymers were dried in vacuo at room temperature for 72h, then weighed to determine conversion. The weight of all polymer isolated, including that from any samples taken, was added together to determine overall conversion. The polymers obtained were off-white gummy solids, which proved soluable in most polar organic solvents.

Results and Discussion

The results obtained are summarized in Table I.

TABLE I

Results of Michael Addition Polymerization

Polymer[a]	Reaction Time (h)[b]	Solvent[c]	Conver. (wt %)	M_n	M_w	M_w/M_n	Tg (C°)
NPG 24	24	MEK	-	11300	231000	20.44	-
NPG 48	48	MEK	-	15000	182000	12.13	-
NPG 96	96	MEK	-	13800	92500	6.70	-
NPG 120	120	MEK	57.5	14200	70000	4.93	-15.1
BAP 24	24	DMF	-	2500	10100	4.04	-
BAP 48	48	DMF	-	3100	10000	3.23	-
BAP 96	96	DMF	-	2800	9400	3.35	-
BAP 120	120	DMF	68.7	5200	11200	2.65	-16.0

a. NPG = Neopentyl glycol bis(acetoacetate) polymers; BAP = N,N'-bis(acetoacetyl)-1,4-piperazine polymers.
b. With the exception of the 120h reaction, reaction times indicate the times samples were taken.
c. MEK - Methyl ethyl ketone, DMF = N,N-dimethylformamide

As in the previous case for the 1,4 and 1,3 benzenedimethanol acetoacetates (1), the initial sample for the NPG based polymer has a very broad molecular weight distribution which narrows considerably over time. As discussed in our previous paper we believe this reflects the system attaining equilibrium. Reaction times in excess of 120h (polymerizations run to 160h, with samples taken at 140h) revealed no further narrowing of the molecular weight distribution and no significant changes in the values of M_n or M_w. The Michael addition reaction is a reversible reaction, particularly in the presence of catalyst (5), so it would not be unreasonable to assume that an equilibrium distribution of species should be eventually obtained.

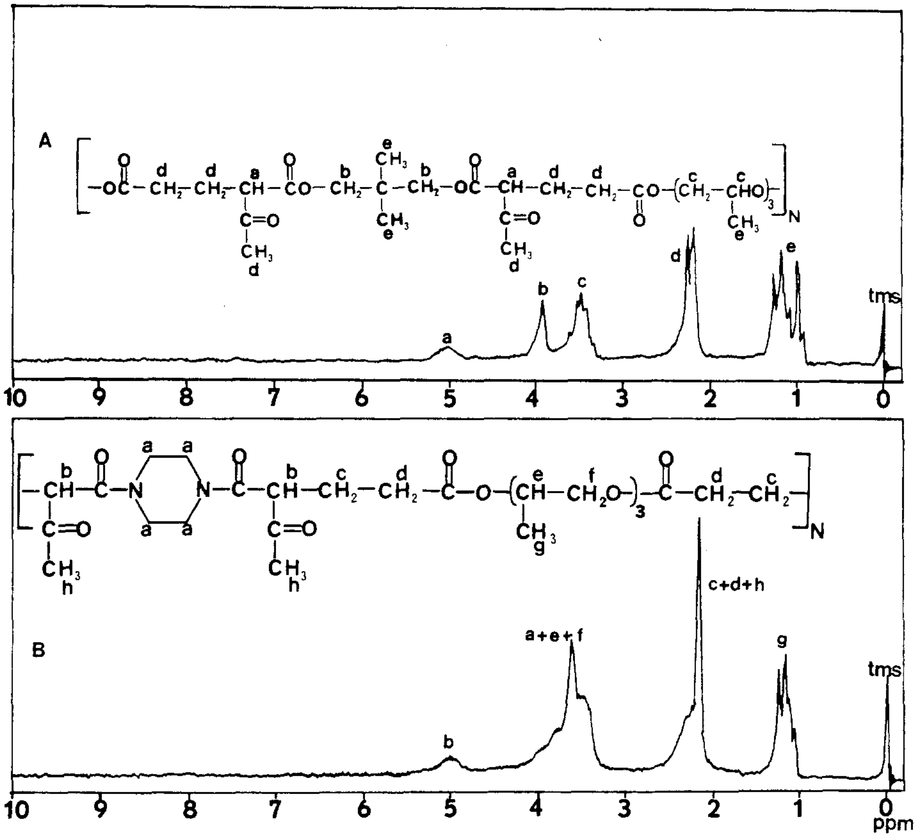

Figure 1. ^{1}H-nmr spectra of; A) NPG based polymer; B) BAP based polymer

The polymerizations conducted with the bis(acetoacetyl) amide show the same behavior as those conducted with bis(acetoacetate) esters, but it is much less pronounced. While the molecular weight distributions are much narrower, the molecular weights obtained are also much lower. It may be that the equilibrium distribution of species is reached very rapidly in the case of the N,N'-bis(aceto-acetyl)-1,4-piperazine based polyemrs and therefore very large chains do not have a chance to be formed as in case(s) of the bis(aceto-acetate) ester based polymers.

Representative ^{1}H-nmr spectra are presented in Figure 1. The assignments are made as shown in the Figure (2,4). Basically, the spectra confirm that the polymers have the structure expected from a consideration of the chemistry involved.

The low Tg's obtained reflect the flexibility or 'softness' of the TPG segment, and are in the range expected for polymers containing 50 mol% of this type of segment (6).

Conclusions

Polymers with broad molecular weight distributions that narrow, in some cases considerably, with reaction time, can be synthesized from bis(acetoacetates) and diacrylates using Michael addition chemistry. The polymers can reach high molecular weight, but have low Tg's. ^{1}H-Nmr confirms that the structure of the polymers is that which is expected.

References

1. D. L. Trumbo, submitted for publication, Polym. Bull., 1990.
2. J. S. Witzeman, W. D. Nottingham and F. D. Rector, Proceeding of the Sixteenth Waterborne and Higher Solids Coating Symposium, 400 (1989).
3. R. S. Clemens and F. D. Rector, J. of Coat. Technol., 61, 83 (1989).
4. S. J. Huang and P. G. Edelman, Polym. Preprints, Vol. 25, No. 2, 63 (1984).
5. E. D. Bergmen, D. Ginsburg and R. Pappo, Org. Reactions, 10, 179 (1989).
6. P. J. Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, Ithaca, NY 1953.

Accepted April 19, 1991 K