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Polymers based on methyl acrylamidoglycolate methyl ether (MAGME): Michael addition – amidation reactions

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Summary

Polymers were synthesized from methyl acrylamidoglycolate methyl ether (MAGME) and various primary amines by utilizing MAGME's electron poor double bond and activated ester functionalities. Generally, the polymerizations proceeded to relatively high conversions but the polymers produced had only low to moderate inherent viscosities and low Tg's. Spectroscopy (IR and ^{1}H-NMR) showed that the polymers had the structure expected from a consideration of the chemistry involved.

Introduction

Michael addition chemistry involves the 1,4 addition of an electron rich species to an electron poor double bond (1):

$$\begin{array}{l} B\!: + CH_2{=}CH{-}X \longrightarrow B{-}CH_2{-}CH_2{-}X \\ \text{where } B\!: = -NH_2,\ -SH,\ -OH \text{ etc.} \qquad (1) \\ X. = -COOR, -CONHR, -CN, -NO_2, \text{etc.} \end{array}$$

Obviously, acrylates and acrylamides, having electron poor double bonds should readily undergo Michael addition reactions with a variety of electron rich species.

Recently, American Cyanamid introduced a substituted acrylamide which contains an activated ester moiety, MAGME (2,3).

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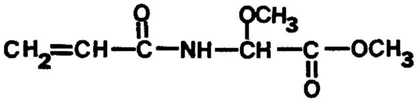


$$CH_2{=}CH-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\overset{\overset{\displaystyle OCH_3}{|}}{C}H-\underset{\underset{\displaystyle O}{\|}}{C}-OCH_3$$

Figure 1
MAGME

The activated ester reacts rapidly with unhindered primary amines at room temperature to form amides. Also, as a substituted acrylamide MAGME has an electron poor double bond; therefore it should be possible to form linear polymers by reacting MAGME with primary diamines. In order to test this hypothesis we undertook the synthesis of polymers by reacting MAGME with various diamines. This report summarizes our findings to date.

Experimental

General

MAGME was obtained from American Cyanamid and was used as received. All the diamines used in this work were reagent grade (Aldrich) and were used as received. All solvents were reagent grade and were used without further purification. Inherent viscosities were measured in DMF at 22°C using a Cannon-Ubbelohde viscometer. The polymer concentrations were 0.7 g/dl. ^{1}H-NMR spectra were obtained at 90 MHz with a Perkin-Elmer R32B spectrometer operating in the CW mode. The spectra were recorded at ambient temperature using CD_3OD as the solvent and TMS as an internal standard. Infrared spectra were obtained on films of polymer cast from ethanol on NaCl plates. The spectrometer used was a Perkin-Elmer 283 IR spectrometer. Glass transition temperature measurements were made on a DuPont 920 DSC, a heating rate of 10°C/min with a nitrogen purge was employed.

Polymer Synthesis

A typical polymer synthesis was performed as follows: MAGME (3.00g, 0.0173 mol) was charged into a 50 ml Erhlenmeyer flask equipped with a magnetic stirring bar, ethanol (8 ml) was added and this mixture was stirred until the MAGME dissolved. 1,6-Hexanediamine (2.10g, 0.0173 mol) dissolved in ethanol (5-6 ml) was added to the MAGME solution as rapidly as possible. The flask was then tightly stoppered and the reaction solution was stirred at room temperature for the desired amount of time. The polymerization was terminated by pouring the contents of the flask into a rapidly stirred 8-fold excess of cold diethyl ether. The polymer was purified by reprecipitation from DMF solution into cold diethyl ether. The reprecipitated polymer was washed with hot THF repeatedly in order to remove any last traces of unreacted monomer. The polymer is a white, gummy solid, which was dried in vacuo at ambient temperature for 72h. Conversion was then determined gravimetrically. All polymerizations were performed in the manner described and all the polymers were white, gummy solids.

Results and Discussion

The results obtained are summarized in Table 1. The values of the properties given are the average of duplicate experiments. All the polymers proved to be insoluable in such common laboratory solvents as $CHCl_3$, CH_2Cl_2, CH_3CN, THF, benzene, toluene and H_2O. The polymers were readily soluable in CH_3OH, C_2H_5OH, DMF and DMSO.

When the diamine used was only sparingly soluable in the reaction solvent (1,8 ODA3 and 1,8 ODAF) no polymer was formed.

Reaction times and solvent type, provided the diamine used was reasonably soluable, had a small effect on polymer yield. In general DMSO and DMF solvents and/or longer reaction times gave somewhat higher yields. Reaction time and solvent had very little, if any, effect on polymer molecular weight. The nature of the diamine used, primary vs secondary, hinder vs unhindered, low molecular weight vs high molecular weight; had a significant effect on polymer yield and/or molecular weight. The highest conversions and some of the highest inherent viscosities, were obtained with the shorter chain, i.e. lower molecular weight, diamines. Secondary diamines and hindered primary diamines (MAPIP and 1,8 MDA respectively) gave the lowest conversions and inherent viscosities. Diamines that were marginally soluable in the reaction medium, such as 1,8-diaminoctane in ethanol, gave lower conversions but not lower inherent viscosities.

The inherent viscosities of all the polymers are low, indicating low molecular weight materials. If the polymerizations are regarded as step growth polymerizations, then the low molecular weights-inherent viscosities are not surprising. The conversions, while high, are not 100%, by using equation 2 (4)

$$\bar{X}_N = \frac{1}{1 - p} \qquad (2)$$

X_N = Number average degree of polymerizaton

P = Extent of conversion

average chain lengths of 2-10 units are calculated for many of the

TABLE 1

Conversions, Reaction Times, Inherent Viscosities and Glass Transition Temperatures for MAGME-Diamine Polymers

Polymer	Amine Comonomer	Solvent	Reaction Temp. (^{o}C)	Rxn Time	% Conv.	η_{inh} (dl/g)	Tg ^{o}C
1,4 DAB	1,4-diamino-butane	Ethanol	22	70h	99.7	0.20	-14
1,3 DAP	1,3-diamino-propane	Ethanol	22	70h	99.1	0.22	-6.5
1,6 HDA1	1,6-diamino-hexane	Ethanol	22	24h	83.3	0.21	-17
1,6 HDA2	1,6-diamino-hexane	Ethanol	22	70h	78.2	0.22	-11.5
1,6 HDA3	1,6-diamino-hexane	Ethanol	23	140h	90.2	0.19	-
1,6 HDA5	1,6-diamino-hexane	DMSO	22	70h	98.6	0.21	-
1,6 HDAF	1,8-diamino-hexane	DMF	22	70h	90.4	0.17	-
1,8 ODA1	1,8-diamino-octane	Ethanol	23	70h	64.6	0.19	-2
1,8 ODA2	1,8-diamino-octane	Ethanol	22	140h	57.9	0.23	-3
1,8 ODA3	1,8-diamino--octane	DMSO	22	70h	No Polym.	-	-
1,8 ODAF	1,8-diamino--octane	DMF	22	70h	No Polym.	-	-
1,8MDA	1,8-menthane-diamine	Ethanol	22	70h	43.5	0.13	-18
MAPIP	Piperazine	Ethanol	22	70h	11.0	0.11	-

are more appropriately classified as oligomers and as such would be expected to give low viscosity solutions (low inherent viscosities). What is surprising is the low inherent viscosities obtained for the 1,4 DAB, 1,3 DAP and 1,6 HDA5 materials. By using equation 2 average chain lengths of 70-300 units are indicated, but these materials are not significantly different in inherent viscosity from many of the other polymers/oligomers obtained in this work.

Several explanations are possible. Inherent viscosity may not be an appropriate method for measuring the relative differences in molecular weight of these materials. Polymers/oligomers with large differences in chain length may have solution property differences that are too subtle to detect by measurement of inherent viscosity. As previously stated, none of the materials produced in this study were soluable in typical GPC solvents (THF, $CHCl_3$ e.g.). Unfortunately we did not have access to a GPC that could be run with DMF or DMSO as the eluent so molecular weight determinations by SEC could not be made.

Alternatively, it could be that these polymerizations should not be regarded as true step growth polymerizations. In fact, given the nature of the Michael reaction (1,5), it is more correct to say that these polymerizations are combinations of 'addition' and step growth polymerizations. A more complete picture of the polymerization mechanism awaits detailed kinetic studies the results of which will be the subject of a future communication.

It may be that some products are formed in the 1,3 DAP and 1,4 DAB polymerizations that are not polymeric but were not removed by the purification procedure used. If these materials were counted as yield, the apparent conversions, hence DP's would seem to be higher than they actually are. However, ^{1}H-NMR gave no evidence of the presence of low molecular weight materials.

Representative IR and ^{1}H-NMR spectra are shown in Figure 2.

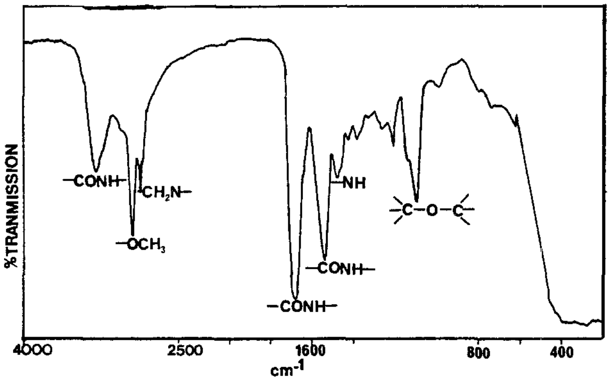


Figure 2A

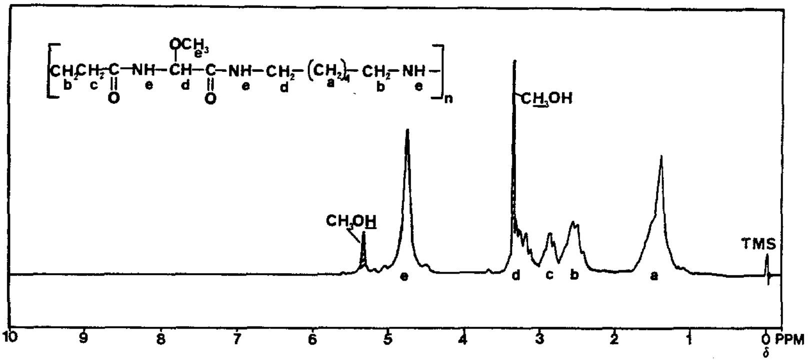
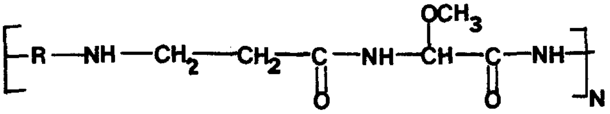


Figure 2B
IR and ^{1}H-NMR Spectra of the 1,6 HDA2 Polymer

The assignments are as shown in the Figure (6-9). Both the IR and ^{1}H-NMR spectra contain the features expected for a polymer that is a polyamine-amide, (Figure 3).

The low Tg's obtained for all the materials also indicate low molecular weights. However, some of the amines used had relatively long aliphatic chains between the amine functionalities and so might be expected to have relatively low Tg's even for moderately high molecular weights. But many of the amines used had short aliphatic chains or ring structures between the amine functionalities which should yield relatively high Tg's provided the materials are of sufficiently high molecular weight (4). This data again suggests low molecular weight materials and the possibility of a non-step growth polymerization mechanism.



$$\left[-R-NH-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-NH-\overset{\overset{OCH_3}{|}}{C}H-\underset{\underset{O}{\|}}{C}-NH-\right]_N$$

Figure 3

Conclusions

Polymers and oligomers based on uncatalyzed Michael addition/amidation reactions between MAGME and various diamines have been synthesized. Inherent viscosity values indicate that all the materials are low molecular weight despite very high conversions in some cases, which may mean that the polymerization does not proceed by a step growth mechanism but by some other mechanism. More detailed work is necessary to completely define this polymerization process.

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