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ARTICLE

Synthesis of glycidyl azide polymer (GAP) via binary ionic liquid – water mixtures without catalyst

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We report the preparation of glycidyl azide polymer (GAP) by the reaction of prepolymer polyepichlorohydrin (PECH) with sodium azide (NaN_3) in mixture solvents of different mass ratios with ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and water without catalyst. The formation of GAP was confirmed by IR and NMR spectroscopy, and the molecular weight of product was traced by gel permeation chromatography (GPC). The conversion of PECH was identified via quantitative ^{13}C-NMR spectroscopy. This method avoids solvent pollution and simplifies reaction post-processing. The reaction was monitored with IR and ^{13}C-NMR. We concluded that the relative solubility of the reaction substrate in the mixed solvents has an important effect on the degree of the reaction.

1 Introduction

Glycidyl azide polymer (GAP) is an excellent material with high density and high nitrogen content. It is an important component in the preparation of high-energy binders.[1-4] In the last few decades, GAP has been prepared with the prepolymer polyepichlorohydrin (PECH) and sodium azide (NaN_3) in organic solvent. Vandenberg and co-workers developed the substitution reaction of PECH with NaN_3 in dimethyl sulfoxide (DMSO) in 1972.[5] Ampleman and co-workers used dimethyl formamide (DMF) as the solvent and synthesized linear GAP with a molecular weight of 2000 g/mol,[6-10] but the organic solvents resulted in environmental pollution and health hazards.

Thus, the development of 'green' organic synthetic methods for GAP is an important and popular research area that can reduce the drawbacks of organic solvents and make the synthetic process simpler while avoiding solvent waste, health hazards and toxicity.[11] Franker and co-workers changed the reaction media to water using tertiary amines or quaternary ammonium salts as the phase transfer catalyst to prepare GAP during azidation.[12] This method enhanced the reaction rate but complicated the post-processing for the emulsification of phase transfer catalyst. Meanwhile, Wagner and co-workers improved the azidation rate with quaternary ammonium, NH_4Cl, LiCl, LiBr as catalysts in DMF. However, they could not simplify the complex post-processing,[13-14] and utilization of catalyst made the reaction complex.

Recently, Joshua Aronson[15] designed ionic liquids (ILs) as the reaction medium due to their low vapor pressure, non-flammability, and high thermal stability. This not only allowed dynamic control[16] but also avoided solvent volatilization. However, the use of pure ILs as the reaction medium for GAP synthesis is undesirable.

The ILs had significant potential for applications in green chemistry—particularly as novel green solvents in organic synthesis.[17] They are widely used for nucleophilic substitution[18-20] and for polymer synthesis because they avoid conventional volatile solvents. In terms of green chemistry, water is the most abundant, cost effective and environmentally benign solvent. Thus we proposed that a mixed solvent using ionic liquids (such as 1-butyl-3-methylimidazolium chloride ([Bmim]Cl)) and water might improve the solubility for the conflicted PECH and NaN_3. This could effectively avoid disadvantages of the traditional organic solvent that might cause environmental, healthy, safety, and equipment corrosion problems. The ionic liquid could be easily separated from the product and used repeatedly.

Here, we described our preliminary results on the synthesis of GAP using PECH with NaN_3 in a mixed solvent of ionic liquid ([Bmim]Cl) and water without catalyst. The reaction processes were followed by IR and NMR spectra. Our method could effectively avoid organic solvent pollution. The protocol is 'green' and simple.

2 Experimental

2.1 Materials

Polyepichlorohydrin (PECH) was synthesized from ethylene glycol with epichlorohydrin (ECH) as monomers and borontrifluoride etherate (BF_3-etherate) as the catalyst (laboratory). Sodium azide (NaN_3, >97%, Xiya reagent), 1-butyl-

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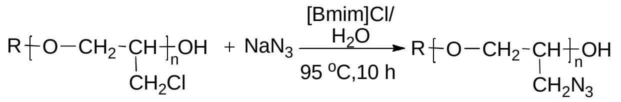
3-methylimidazolium chloride ([Bmim]Cl, >97%) and distilled water were used without further purification.

2.2 Synthetic procedures

The GAP synthesis was carried out in a 250 ml three-necked round bottom flask equipped with a thermometer, a reflux condenser, and a mechanical stirrer. The 30.00 g of PECH was dissolved in mixed solvents with a different mass ratio of [Bmim]Cl and distilled water and stirred. The solution was heated to 95°C in an oil bath, and then 21.09 g of sodium azide was rapidly added into the reaction mixture with continued stirring for 10 h at this temperature. The reaction was monitored with quantitative ^{13}C-NMR. After the reaction finished, the mixtures were washed sequentially with distilled water more than 3 times until all salts were removed. The water was then evaporated to recover the products.

Table 1 Synthesis of GAP



Ent	[Bmim]Cl/H_2O[a]	T (°C)	t (h)	Yield (%)[b]
1	4:1	95	10	89.17
2	5:1	95	10	56.52
3	100:0	95	10	50
4	1:1	95	10	45.7
5	2:3	95	10	37.5
6	1:4	95	10	24.82
7	0:100	95	10	0

[a] Mass ratio [b] Isolated yields.

2.3 Characterization

The infrared spectra of polymers were recorded using a VERTEX70 FTIR spectrometer from 500-4500 cm^{-1}. The ^{1}H-NMR and ^{13}C-NMR spectra of polymers were measured using a BRUKER 400 MHz NMR spectrometer in $CDCl_3$ solvent with tetramethylsilane as the internal standard.

3 Results and discussion

The hydroxyl-terminated GAPs were prepared by reacting the corresponding polyepichlorohydrin with sodium azide in different mixed solvents of 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and water at 95°C for 10 h (in Table 1). The products were amber/dark colored liquids with molecular weights of 3300-3600 g/mol.

The ^{1}H-NMR spectral analysis suggested that GAP synthesis was achieved. The ^{1}H-NMR spectrum of PECH showed main characteristic peak at 3.8 ppm due to (-OH), 3.5 ppm (Hc) due to $-CH_2$-Cl protons of PECH pendants, and 3.65 ppm (Ha, Hb) due to the protons of the $-CH_2$, -CH groups of polyether main chain of PECH. The ^{1}H-NMR spectrum of GAP1 (entry 1 in Table 1) shows peaks at 3.25 ppm (Hc) corresponding to the methylene protons of the pendant azidomethyl groups ($-CH_2N_3$) of GAP1 and at 3.45-3.55 ppm (Ha, Hb) belonging to the methylene protons of polyether main chain of GAP1, which is also at 3.8 ppm (Hd) due to (-OH). The ^{1}H-NMR spectra of PECH and GAP1 are presented in Figure 1.

Fig. 1 ^{1}H-NMR spectra of GAP1 and PECH in $CDCl_3$

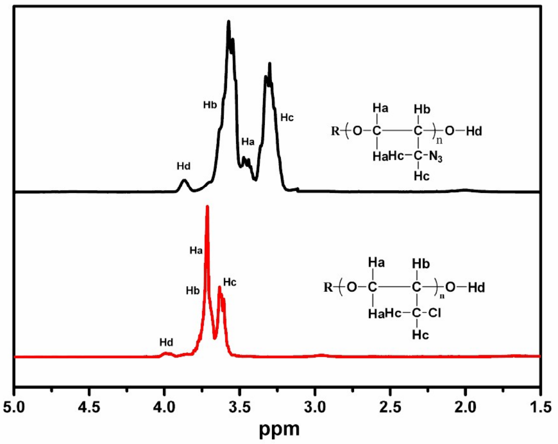
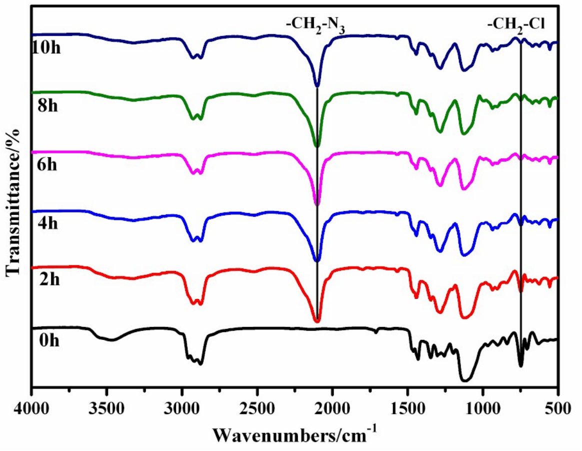


Fig. 2 IR spectra of GAP1.



The formation of GAP1 was also confirmed by the characteristic peaks obtained in the IR and ^{13}C-NMR spectra. The IR spectra of GAP1 showed characteristic peaks at 1280 and 2100 cm^{-1} corresponding to the formation of the azide group in the polymer chain. The $-CH_2$-Cl peak (746 cm^{-1}) is still present in Fig. 2. The presence of the strong prominent peaks corresponding to $-CH_2-N_3$ and the intensity of the $-CH_2$-Cl absorption band became weaker and weaker (but still existed) in the reaction progress. This indicated the formation of GAP, but not completely. The IR spectra of other GAPs are in the SI.

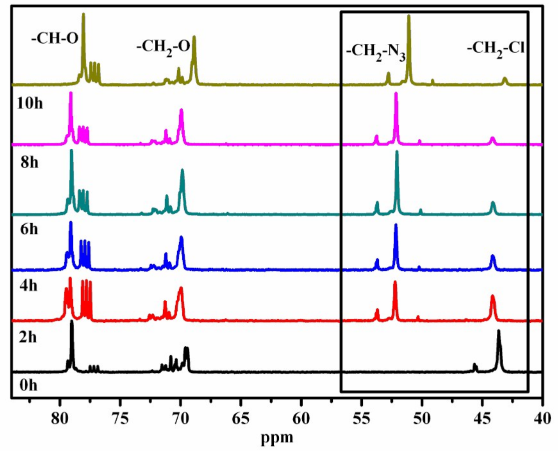


Fig. 3 ^{13}C-NMR spectra of GAP1 in CDCl$_3$.

Products with different side groups (-CH$_2$-Cl or -CH$_2$-N$_3$) were identified by the ^{13}C-NMR spectra as shown in Figure 3 (the others are in SI). The common peaks for the GAPs were around (δ) 69.5-71.5 ppm (-CH$_2$-O) and 76.5-80.5 ppm (-CH-O). In addition to these peaks, the characteristic peaks at 42.5-44 ppm are attributed to -CH$_2$-Cl and those at 51-54 ppm are attributed to -CH$_2$-N$_3$. The ^{13}C-NMR method analyzed the quality of the products, and could be used to make PECH conversion curves as a function of time (Fig. 4). There was no GAP when pure water was the solvent. This inferred that the reaction did not occur. The result was also undesirable when the reaction was carried out in [Bmim]Cl. Figure 4 shows the yield of GAP synthesized in mixed solvents of different mass ratio of [Bmim]Cl and water. The highest transformation was obtained when the mass ratio of [Bmim]Cl and water was 4:1.

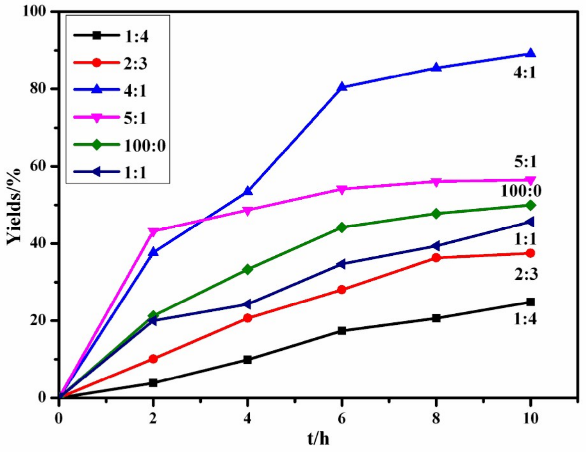


Fig. 4 Yields of GAPs in mixture solvents of different mass ratio of [Bmim]Cl and water.

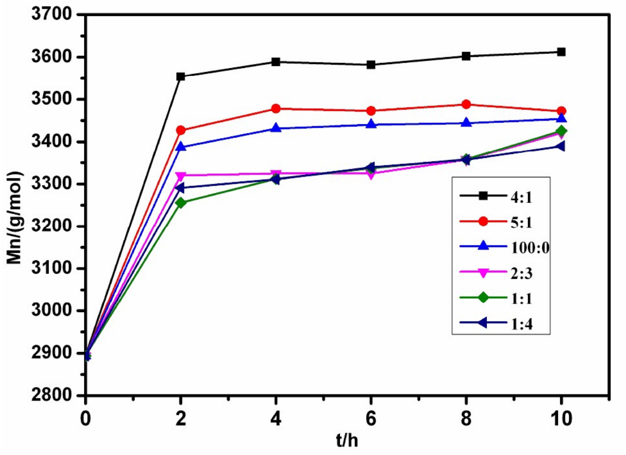


Fig. 5 GPC of GAPs produced in binary solvent mixtures with different mass ratio of [Bmim]Cl and water.

GPC traces for the products are shown in Figure 5. The number-average molecular weight (Mn) was from 3300 to 3600 g/mol, and the polydispersity (PD) was about 1.22. The Mn increased rapidly during the first two hours of the reaction; this growth slowed down gradually and eventually plateaued. The maximum value of molecular weight was from mixed solvents of [Bmim]Cl and water with a mass ratio of 4:1. This inferred that this condition most effectively caused azidation of PECH via NaN$_3$.

The molecular weight is lowest at a mass ratio of mixed solvents of 1:4. This suggested that this system had the smallest proportion of nucleophilic substitution of PECH with NaN$_3$ in the reaction. However, the GPC data supports the results of the yields of GAP in mixed solvents of [Bmim]Cl and water with different mass ratios.

These results are because PECH could not dissolve in water. Thus, there is no opportunity to react with NaN$_3$. However, NaN$_3$ dissolves easily in water, but [Bmim]Cl is only slightly soluble. Thus, there is no GAP in water, and the result was also undesirable in [Bmim]Cl. The mixed solvent facilitated high yields, and the transformation and rate of reaction changed. The GAP yield from reactions using different mass ratios of [Bmim]Cl and water was different. The highest transformation was obtained at a mass ratio of [Bmim]Cl and water of 4:1. The solubility of the reactants in the mixed solvent of [Bmim]Cl and H$_2$O played a important role. This binary ionic liquid and water mixture have unique solvent polarity and hydrogen bond character. This influenced the reaction, and the results are due to combination effects.

4 Conclusions

In summary, GAPs were prepared in mixed solvent with different mass ratios of [Bmim]Cl and H$_2$O by azidation of the corresponding poly(epichlorohydrin)s with sodium azide. The yields were confirmed with IR and ^{13}C-NMR spectral analysis. The synthesis of GAP in pure water or [Bmim] Cl was undesirable, and thus the solvents with different mass ratios of

[Bmim]Cl and H_2O were shown to influence the rate and the extent of the reaction. As the mass ratio increased, the rate and the extent of the reaction rose, but further increases showed no further benefit. However, we did find an optimum mass ratio of [Bmim]Cl and H_2O for preparing GAP in high yields. This simple and ‘green’ ionic liquid-water mixed solvent system is catalyst-free. It effectively avoids organic solvent pollution problems. Further synthesis in mixed solvents of water and ionic liquids with different anions is underway.

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Graphic:

Synthesis of glycidyl azide polymer (GAP) via binary ionic liquid–water mixtures without catalyst

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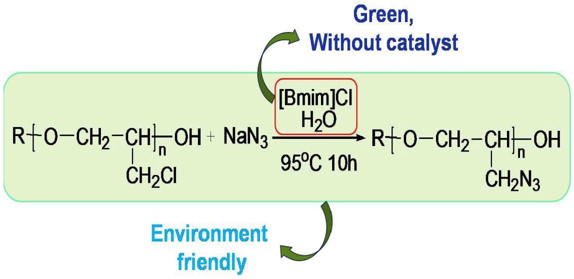

A simple ionic liquids-water mixed solvent system without catalyst for the synthesis of GAP was reported, which could effectively avoid organic solvent pollution.