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Synthesis of α-hydroxy-ω-amino poly(ethylene oxide) and its use in reaction injection moulding (RIM)

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SUMMARY

Computer simulations show that oligomers with two different terminal groups with dissimilar reactivities for isocyanates give a delayed viscosity rise in polyurethanes. This is a desired behaviour for RIM processes. Therefore, an α-hydroxy-ω-amino poly(ethylene oxide) (HAPEO) has been prepared. The synthesis was carried out by the ethoxylation of 2-hydroxyethyl phthalimide as a blocked amine. Hydrazinolysis appears to be the best way to obtain the deblocked oligomer. The product properties were compared with an oligomeric diamine ether (Jeffamine D2000). The gel time of HAPEO (M_n = 500) and JAD2000 (M_n = 2000) was the same (2 sec.). The product with HAPEO had a higher modulus, a comparable impact and tensile strength and a lower elongation at break.

INTRODUCTION

Reaction injection moulding (RIM) is an important processing technique, in particular for polyurethanes. The cycle time of thermosets produced with this technique is about the same as for injection moulded thermoplasts. The starting materials of RIM are low viscous liquids which are transformed into a three dimensional network in about two minutes. The gelation has to take place in a relatively short time interval. This imposes severe requirements on the chemistry of such a system. In structural RIM (SRIM) these requirements are even more severe, because the mould is partly filled with glass fibers. The initial viscosity must, therefore, be low and stay low as long as wetting out is not complete. However, subsequently the polymerization rate should be very high. Thus, one needs a reactive system in which the viscosity rise due to gelation is postponed until a high degree of conversion is reached. Yet, an acceptable level of cure is required in the end product.

At the moment, RIM polyurethanes are composed by reacting an isocyanate with a polymeric polyol and a chain extender. The latter is often a low molecular hindered aromatic diamine [1]. In order to obtain faster systems, polyureas are often employed. However, these systems are so fast that they are difficult to process [2]. Polymeric diamines (e.g. Jeffamines) are processable if the molecular mass is not too low. However, in order to obtain products with high matrix moduli (SRIM), low molecular mass prepolymers are preferred.

We report here the synthesis of α-hydroxy-ω-amino terminated polyethers (HAPEO) and their application with isocyanates in polyurethane thermosets in order to establish whether these products can fill the gap between the

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polyurethanes and the polyureas. The amine group of the HAPEO reacts very fast with an isocyanate but will still give low molecular mass products since mainly di- and trimers are formed initially. Until a conversion of about 50 % of the isocyanate groups, it is expected that the molecular mass remains relatively low. In the second stage of conversion, the polymerization continues by reactions between the hydroxy terminated reaction products and the remaining isocyanates. This results in gelation and network formation, but at a higher conversion than when a diamine is used instead of HAPEO.

EXPERIMENTAL

Phthalimide blocked α-hydroxy-ω-amino poly(ethylene oxide)

2-Hydroxyethyl phthalimide (HEP) was prepared according to Billman [5]; 579.5 g of HEP and 3.63 g $NaOCH_3$ were heated to 140 °C. The methanol was removed by repeated vacuum distillation. The ethoxylation was performed at 170 °C during 2 hours under a pressure of about 3 bar. In that period about 10 monomeric units are polymerized. Higher molecular masses can be obtained by extending the reaction time.

α-Hydroxy-ω-amino poly(ethylene oxide)

100 g of the phthalimide blocked α-hydroxy-ω-amino poly(ethylene oxide) was dissolved in 200 ml ethanol. 9.2 g of a hydrazine hydrate (55%, equimolar) was added and the mixture was refluxed for 30 minutes. Next, 15 g concentrated HCl was added. Immediately a yellow precipitate appeared. The precipitate was removed by filtration at 0 °C. The filtrate was neutralized with NaOH and the NaCl formed was filtered off. The oligomer was isolated by evaporation.

Reaction injection moulding

A smale scale apparatus (RCM-800 machine, Hi-Tech Engineering) was used to carry out the RIM experiments. A mixture of the oligomer and the diethyltoluene diamine (DETDA) and the catalyst was one stream, while the diisocyanate formed the other one. The oligomer tank was kept at 60-75 °C under 3-5 bar pressure of dry nitrogen. The diisocyanate was held at room temperature. The impingement mixing head pressure was about 100 bar. The flow rate was 40 g/s at 60-90 °C and the shot time 0.7 s. After the injection, the sample slab was post-cured in the closed mould for 1 hour at 120 °C.

RESULTS AND DISCUSSION

The formation of networks through mixtures of difunctional resins with di- and trifunctional crosslinkers has been modeled with computer simulations by one of us [3]. This model was originally developed for reactions between molecules containing the same reactive group within each molecule. However, it is possible to introduce substitution effects for some of the functional groups. A negative substitution effects means, that the second group reacts slower after the first one has reacted. The larger the negative substitution effect the larger the difference in reactivities. The actual difference in reactivity between an aliphatic amine and an alcohol with an isocyanate is more than a factor of thousand [2,4].

We used this model to estimate the increase of the molecular mass as function of the isocyanate conversion. The reactivity ratio between an amine and an alcohol with an isocyanate was chosen to be 1000. A larger difference has no more influence on the results. The functionality of the HAPEO was set at two. This implies that biuret formation was neglected. The functionality of the isocyanate was taken to be 2.3, which is a typical value for commercial systems. The molecular mass of the HAPEO and the isocyanate was set at 1500 and 300, respectively.

In Fig. 1 two curves are shown, calculated with the aforementioned network model [3]. The R curve is calculated on the basis of equal reactivities, typical for either diamines or diols with a molecular mass of 1500 as well. The S curve is based on a model HAPEO, i.e. an oligomer with a negative substitution effect of 10^{-3}. In the S curve, the molecular mass of the product reaches the sum of the isocyanate and the HAPEO at 50 % conversion of the isocyanate and 100 % of the amine. This is, on the average, what one expects with such a large difference in reactivities. After this point, the polymerization continues with the urethane formation. Because the average functionality is larger than two, the product will finally be crosslinked. The postponed gelation as function of the conversion is obvious from these calculations. With the model the ultimate network structures were verified to be equal. This theoretical result urged us to look for a synthetic route to produce these oligomers.

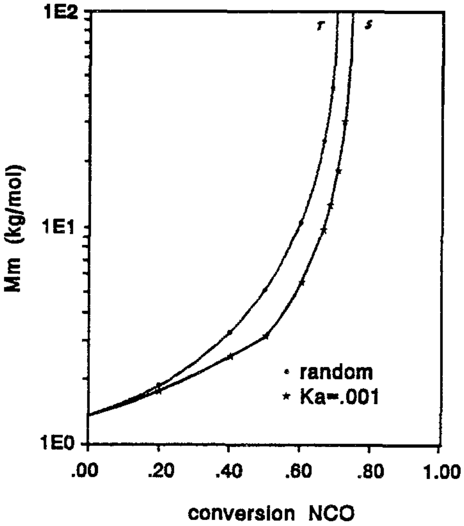


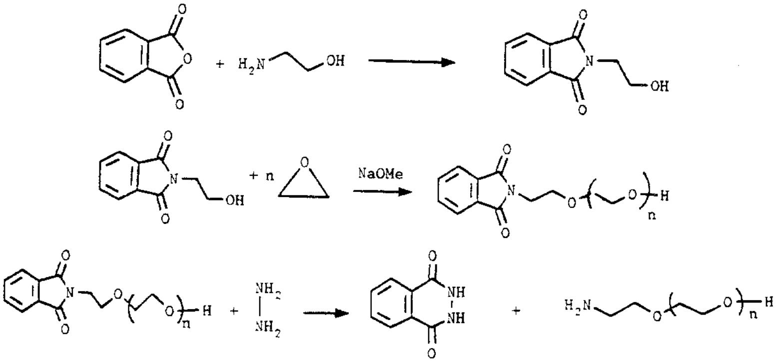
Fig.1.
Calculated mass average molecular mass of the polyurethane as function of the conversion of the diisocyanate.

There are several routes to synthesize HAPEO. One way is to transfer a polymeric diol or diamine into a HAPEO. For instance, one could react a diol with acrylonitrile and hydrogenate the resulting product. Another route is to react a diamine with a caprolactone. However, this results always in a mixture of products which is difficult to purify.

We have chosen to start with ethanolamine in which the amine group was blocked. Ethanolamine reacted readily and quantitatively with phthalic anhydride to form an imide, see scheme 1 [5]. Next, the polyether was prepared by the ethoxylation of the imide with ethylene oxide (EO). The initiator was obtained by treating the imide with sodium methoxylate. The methanol formed was removed by evaporation. EO was dosed to the molten initiator at about 150 °C. The ethoxylation proceeded in 2 hours at 3 bar pressure. The product had a dark brown colour. The degree of ethoxylation depends on the amount of EO added. Two products were prepared, one with on average of 10 additional EO`s and one with 21 additional EO`s.

<u>Scheme 1.</u>

Reaction scheme of the synthesis of α-hydroxy-ω-amino poly(ethylene oxide)



The imide protecting group is not completely insensitive to the alkaline conditions used during the ethoxylation. According to the ^{1}H-NMR spectrum (Fig. 2) about 10 % of the phthalimide has been opened during the ethoxylation. The peaks between 7.6 and 7.7 ppm are assigned to the ring opened product. This can give by-products because the formed carboxylate anion can also be ethoxylated.

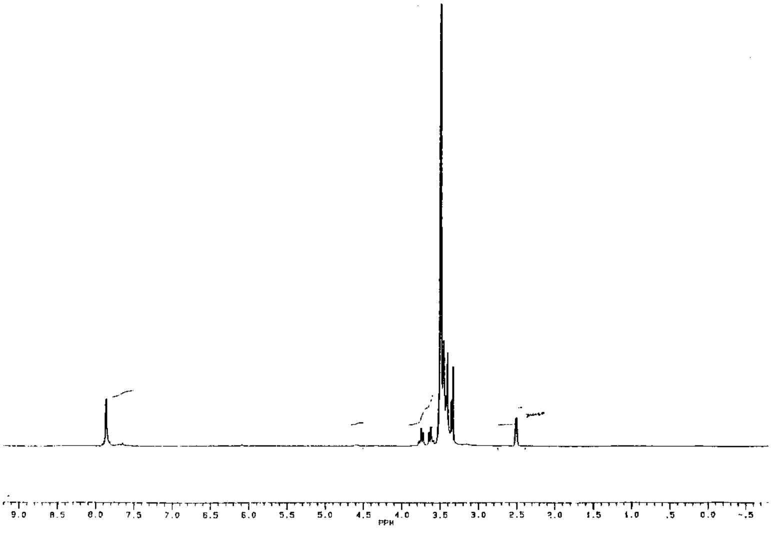


Fig. 2. ^{1}H-NMR of the phthalimide blocked α-hydroxy-ω-amino poly(ethylene oxide) (M_n = 500).

The deblocking reaction was performed with the product as obtained. Several deblocking reactions were at our disposal. The alkaline hydrolysis was rejected because this might degrade the poly(ethylene oxide) [6]. Aminolysis with methylamine in water gave a solid which was difficult to handle and to purify [7]. The hydrazinolysis appears to be the best choice [8]. The reaction is rather fast (0.5 hour) in ethanol as solvent. The hydrazine phthalimide was removed by precipitating the HCl salt. After filtration the HAPEO was neutralized and isolated by evaporation of the solvent in a 85% yield. This product was tested in a RIM recipe and compared with Jeffamine D2000, an α-ω-amine terminal poly(propylene oxide) (PPO) with a molecular mass of about 2000. The results are given in Table 1.

Table 1. Polyurethane-urea RIM systems based on JAD2000 and HAPEO 500.

Reagent	JAD2000	HAPEO 500
Amine Eq. Wt. (g)	1000	500
Oligomer (g)	42.57	39.11
DETDA 1) (g)	18.94	13.87
Dabco T-12 2) (g)	0.03	0.024
Dabco 33 LV 3) (g)	0.06	0.052
UL-28 4) (g)	0.03	0.024
Isonate 143L 5) (g)	38.37	46.92
Oligomer/DETDA/Isonate 6)	1/5/6.3	1/1/2.1
Gel time (s)	2	2
Hardness shore D	68	75
Tensile strength (MPa)	26.4	26.1
Young's modulus (MPa)	31.9	55.8
Elongation (%)	53	28
Flex. strength (MPa)	24.1	59.4
Flex. modulus (MPa)	455	1027
Izod (J/m)	258	250

1) Diethyltoluenediamine, 2) dibutyltin dilaurate, 3) triethylenediamine in dipropylene glycol, 4) tin carboxylate, 5) carbodiimide modified MDI and 6) molar ratio.

The results show that the gel time for both systems was 2 seconds in spite of the higher concentration of reactive groups in HAPEO. This gel time is in the desired range for RIM. Faster systems are difficult to process. The HAPEO however, has only a molecular mass of 500 while the molecular mass of the JAD 2000 is 2000. This difference is clearly reflected in the modulus of the product, which is about twice as high for the HAPOE product. The elongation at break is lower, as expected. Fortunately, the impact and tensile strength are in the same range as with JAD2000. The difference between the flexural and the tensile strength for the HAPEO system is not clear. In structural RIM applications, a great advantage is expected from the HAPEO system, because of the lower starting viscosity and the resulting better wetting out of the glass fibers

CONCLUSIONS

The idea that the gel point of a reactive system can be delayed by using an oligomer with reactive groups of very much different reactivities was verified theoretically and experimentally. According to the theory, the ultimate network structure is not affected by the difference in reactivities.
An α-hydroxy-ω-amino poly(ethylene oxide) (HAPEO) was prepared by ethoxylation of 2-hydroxyethyl phthalimide. The blocking group was removed by hydrazinolysis. With this oligomer polyurethanes were prepared by reaction injection moulding (RIM). The results were compared with polyureas made with Jeffamines (oligomeric diamines). With HAPEO (M_n = 500 g/mol) the same gel time was obtained as with JAD2000 (M_n = 2000 g/mol), although the concentration of reactive groups is much higher. As expected, the modulus was higher and the elongation at break lower. The tensile strength was about the same. Thus, the possibility to use HAPEO with lower molecular masses than comparable diamines to produce polyurethanes with the same gel time, was experimentally confirmed.

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