New Catalysts for Urea Formation Reaction. I. Effect of Catalyst on Molecular Weight of Polyureaurethane and Determination of the Minimum Demolding Time

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Synopsis

2-Methyl benzoic acid as a new catalyst for urea formation reaction has a significant effect on the molecular structure of polyureaurethane. For instance, it increased molecular weight of polyureaurethane, but decreased chemical crosslink density. The minimum demolding time (DT) of polyureaurethane as an index of catalytic activity was also discussed based on the mechanical properties. DT is defined as the torque time for a mixture of curative and prepolymer to reach 90% of its nearly final value. A marked increase in extension ratio at break (E_B) before DT was partially attributed to intermolecular entanglements which arose at molecular weights higher than 4500 [rheological critical molecular weight of poly(oxytetramethylene)glycol]. Primary aliphatic amines in amide solvents selectively cleaved biuret or allophanate bonds of polyureaurethane. This helped to determine molecular weight of crosslinked polyureaurethane.

INTRODUCTION

Although urea-forming reaction is faster than a urethane-forming one, it is important to shorten the demolding time of polyureaurethane, by using catalysts. The fact that benzoic acid accelerates urea-forming reaction[1] led us to investigate catalytic activities of various carboxylic acids to find more active catalysts. Mechanical properties for polyureaurethane prepared with these new catalysts will be reported in a subsequent article.[2] One of the purposes of this article is to study the effect of the catalyst on the molecular structure of polyurearethane, i.e., molecular weight and chemical crosslink density. Another is to propose a method for determining the minimum demolding time (DT).

Crosslinks may be formed in polyurearethane from a diisocyanate compound and a chain extending agent having difunctional active hydrogen groups. It is due to biuret and allophanate linkages. Such crosslinks should be cleaved before determining the molecular weight of polyureaurethane. The crosslinks are thermally unstable and are apt to disasociate at high temperature.[3] They can be more quantitatively cleaved by reaction between aliphatic amine and biuret or allophanate bonds[4]:

$$\text{—NHC—N—C—NH—} + RNH_2 \rightarrow \text{—NHCNH—} + \text{RNHCNH—} \qquad (1)$$

(biuret)
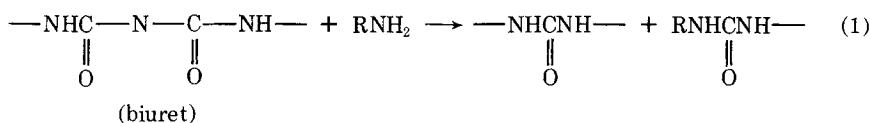
EXPERIMENTAL

Materials

n-Butyl amine, di-n-butyl amine, dimethylformamide (DMF), dimethyl-acetamide (DMAc), and tetrahydrofuran (THF), reagent-grade materials, were used as received. Coronate 4090 from Nihon Polyurethane Co. Ltd. was used as an isocyanate-terminated prepolymer derived from 1 mole of poly(oxyte-tramethylene)glycol (PTMG) and 2 mole of 2,4-tolylenediisocyanate. The content of isocyanate group (NCO content) was 4.12% by weight. 3,3'-Di-chloro-4,4'-diaminodiphenylmethane (MOCA) was used as a chain-extending agent. Molar ratios of amino groups of MOCA to isocyanate groups of the pre-polymer were varied from 0.8 to 1.1. 2-Methyl benzoic acid previously dissolved in melted MOCA was used as a catalyst. The mixture of the prepolymer and MOCA was cast in a slab mold, and cured at 100°C for 180 min when no catalyst was employed, and for a period corresponding to the minimum demolding time when the catalyst was employed. Postcure was done for seven days under 50% humidity atmosphere at 30°C.

Measurements

Chemical crosslink density (νc) proposed by McGillvary[5] is one of the important factors affecting mechanical properties, such as tear energy, for poly-ureaurethane. It was determined by Cluff's method[6] from a correlation between compressive strain and stress:

$$f = \nu_c RT \,(\alpha - \alpha^{-2}) V_R^{-1/3} \tag{2}$$

where f is force per unit area of an unswollen sample required to compress a swollen sample to compression ratio α, R is the gas constant, T is the absolute temperature, and V_R is volume fraction of polyureaurethane in the swollen sample. It was measured by a Reticurometer by Wallace Inc., after a test piece in the form of a disk, 6 mm in diameter and 2 mm thick, had been swollen over-night in THF.

Intrinsic viscosities ([η]) were measured at 30°C in THF or DMAc–amine solution. Cure curves were measured at 100°C by a Curastometer[7] by Japan Synthetic Rubber Co. Ltd. Tensile strength at break [T_B (kg/cm^2)], extention ratio at break [E_B (%)], and 10% modulus [M_{10} (kg/cm^2)] were measured at 100°C immediately after test pieces were cut from slab sheets with a ring dumbbell at various stages of cure. Simultaneously, a part of each test piece was immersed in 10% by weight solution of n-butyl amine in DMAc to deactivate isocyanate groups. n-Butyl amine and DMAc were then evaporated to be replaced by THF, accompanied by measurement of intrinsic viscosities and calculation of molecular weight (MW) according to[8]

$$[\eta] = 6.26 \times 10^{-4} \text{MW}^{0.71} \tag{3}$$

RESULTS AND DISCUSSION

We studied effect of amine concentration on the time (t_s) for crosslinked polyureaurethane to be solubilized completely in n-butyl amine–DMAc solution. Polyureaurethane employed had a NH$_2$/NCO ratio of 0.80 and ν_c of 2.04×10^{-4}

mole/cm^3 and the test pieces were 1-mm cube and 2 mm^3, respectively. For each test piece t_s is decreased with increasing amine concentration and showed a linear correlation with reciprocal of amine concentration (Fig. 1). The slopes for the two test pieces, however, are not identical.

Assuming the reaction of amine with biuret or allophanate bond is of a second order, the reaction equation will be written

$$-\frac{d[X]}{dt} = k[X][A] \qquad (4)$$

where [X] is the concentration of biuret or allophanate bond, [A] is the concentration of amine, and k is a rate constant. Equation (5) can be obtained by integrating eq. (4) with respect to time, since [A] is much larger than [X] and is considered to be nearly equal to its initial value $[A]_0$,

$$t_s[A]_0 = (1/k) \ln ([X]_0/[X]t_s) \qquad (5)$$

where $[X]_0$ and $[X]t_s$ are [X] at $t = 0$ and t_s, respectively. Owing to heterogeneous reaction in the solid–liquid system, the lines (Fig. 1) do not pass the zero point contrary to expectations from eq. (5), the 1 mm-cubed piece is uncrosslinked faster than the 2 mm-cubed sample.

In order to see the effect of kinds of solvents on the rate of uncrosslinking, t_s for the 2 mm-cubed piece (Fig. 1) was determined in 10% by weight solution of n-butyl amine in THF, DMF, and DMAc. Although THF is a good solvent for polyureaurethane, t_s determined in THF is as long as 24 hr, while t_s in DMF and DMAc are only 5.0 and 5.1 hr, respectively. Amide solvents are preferred for rapid solubilization of crosslinked polyureaurethane.

Aliphatic amines may also cause scission of main chains, which interferes with the molecular weight determination of polyureaurethane. The change in intrinsic viscosity of polyureaurethane is followed with time in aliphatic amine–amide solvent solution. Polyureaurethane employed had a NH_2/NCO ratio of 1.1 and no crosslinks. The rate of decrease of the intrinsic viscosity in the n-butyl amine solution after 50 hr is only 5% (Fig. 2), while that in the di-n-butyl amine solution is more than 30%. A reaction between amino group and urea or urethane group occurs in the di-n-butyl amine solution. Secondary aliphatic amines of stronger basicity therefore seem unsuitable for our purpose.
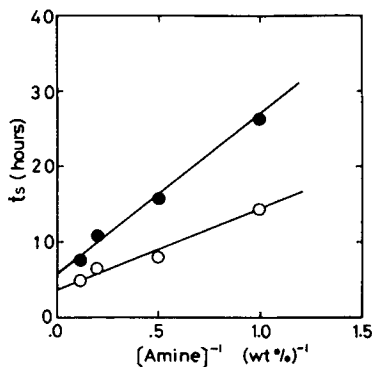

Fig. 1. Relationship between solubilizing time (t_s) of crosslinked polyureaurethane and reciprocal of amine concentration. (●) 2 mm cubed; (○) 1 mm cubed; Solution: n-butyl amine-DMAc; amount of polyureaurethane: 3 g per 100 g of the solution; ν_c for polyureaurethane: 2.04×10^{-4} mole/cm^3.
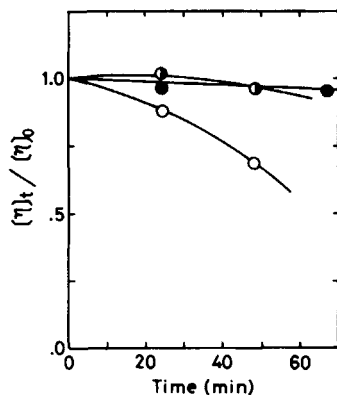
Fig. 2. Change of intrinsic viscosity of polyureaurethane in amine-amide solvent solution with aging time at 30°C. Amount of polyureaurethane: 3 g per 100 g of the solution; polyureaurethane employed had no crosslinks. Amine concentration: 10 wt %; (●) n-butyl amine-DMAc; (◑) n butyl amine-DMF; (○) di-n-butyl amine-DMF.

Effect of Catalyst on Molecular Structure of Polyureaurethane

The maximum amount of polyureaurethane that can be dissolved in amine–amide solvent depends on both amine concentration of the solution and chemical crosslink density (ν_c) of the polyureaurethane. This was studied using polyureaurethanes having various values of ν_c made with and without 2-methyl benzoic acid. The chemical crosslink density was varied by changing the NH_2/NCO ratio. The solubility of polyureaurethane with the catalyst decreases with increasing ν_c (Fig. 3). When the polyureaurethane is employed in higher amount than open circle (Fig. 3), it only swells until it absorbs all of the solution and fails to be solubilized. On the contrary, polyureaurethane without catalyst is much more easily solubilized; the maximum soluble amount is larger than 13% by weight regardless of ν_c. This indicates some difference in molecular structure between the two polyureaurethane systems.

The ν_c for each polyureaurethane is plotted against NH_2/NCO ratio (Fig. 4). The chemical crosslink density is zero at NH_2/NCO ratio of 1.1, but increases
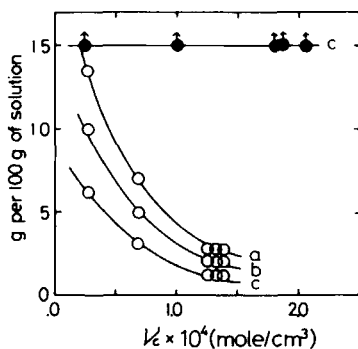

Fig. 3. Relationship between the maximum soluble amount of polyureaurethane in n-butyl amine-DMAc and the chemical crosslink density. Amine concentration (——): (a) 50 wt %, (b) 30 wt %, (c) 10 wt %; (○) polyureaurethane with 4.12 mmole of 2-methyl benzoic acid per 100 g of prepolymer; (●) polyureaurethane without catalyst; arrows mean that more than 15 g of polyureaurethane can be solubilized.
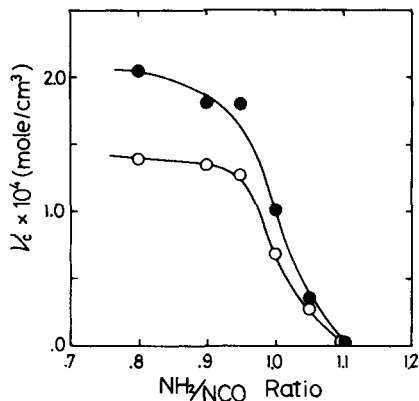
Fig. 4. Relationship between chemical crosslink density and NH_2/NCO ratio of polyureaurethane. (O) Polyureaurethane with 2-methyl benzoic acid; (●) polyureaurethane without it.

with decreasing ratio. The ν_c for polyureaurethane with catalyst is smaller than that without catalyst at any NH_2/NCO ratio, because the crosslink reaction is suppressed under the acidic condition.[9] Therefore, polyureaurethane with the catalyst can be expected to have a larger molecular weight.

The samples (Fig. 4) were dissolved in n-butyl amine–DMAc solution, followed by measurements for intrinsic viscosity. The $[\eta]$ for polyureaurethane with the catalyst is substantially larger than that without the catalyst (Fig. 5). This result, in agreement with the result (Fig. 4), can best explain the decreased solubility of the polyureaurethane with the catalyst as a molecular effect. The $[\eta]$ (Fig. 5) is increased monotonously with decreasing NH_2/NCO ratio, though it should theoretically have a maximum at the ratio of 1.0,

$$MW \propto \frac{1}{|1 - \gamma|} \tag{6}$$

where γ represents the NH_2/NCO ratio. The discrepancy arises from consumption of isocyanate groups during postcure by crosslinking and reaction with
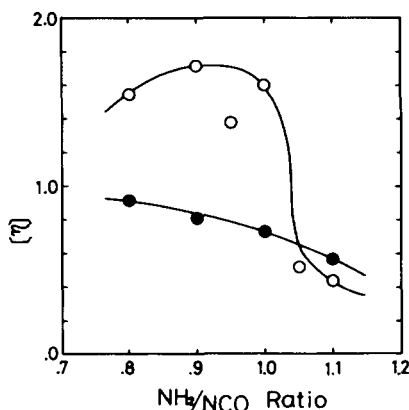

Fig. 5. Relationship between intrinsic viscosity and NH_2/NCO ratio of polyureaurethane. (O) Polyureaurethane with 2-methyl benzoic acid; (●) polyureaurethane without it; $[\eta]$ was measured in THF at 30°C.

moisture. Actually, the conversion of isocyanate groups after demolding are 95.7 and 97.0% for polyureaurethanes at NH_2/NCO ratio of 1.0 with and without the catalyst, respectively. Most of the remaining isocyanate groups are deactivated by the above-mentioned reactions, though conversion over 99% by chain extension reaction is required to achieve high molecular weight.

Minimum Demolding Time

Minimum demolding time (DT) will be used in a subsequent paper[2] as an index of catalytic activity. When polyureaurethane is demolded, it must be strong enough at cure temperature to resist deformation and stress encountered during demolding. Thus, DT should be defined based on measurements of mechanical properties. Figure 6 shows several mechanical properties for polyureaurethane at 100°C and at various cure times. The E_B (elongation at break) increases very sharply between 60 and 90 min and reaches a constant value thereafter. Point A (Fig. 6) is, therefore, regarded as the minimum demolding time. In fact, at this point, T_B (tensile strength at break) and M_{10} as well as E_B approach their final values.

The experiment (Fig. 6) is, however, so troublesome that another convenient method is favored in order to determine DT. A determination of the cure curve
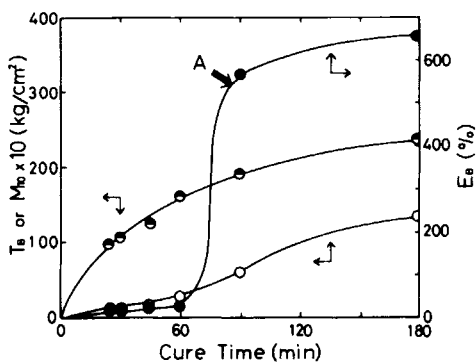

Fig. 6. Mechanical properties at 100°C and at various stages of cure. NH_2/NCO ratio of polyureaurethane employed was 1.0. (◓) M_{10}; (○) T_B; (●) E_B.
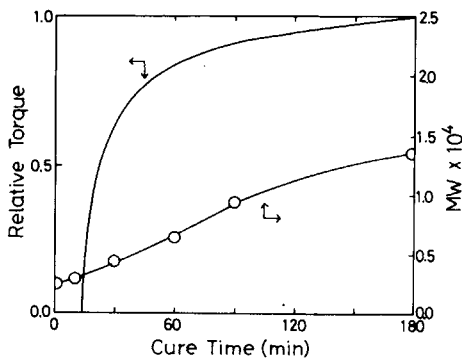

Fig. 7. Changes of torque and molecular weight of polyureaurethane with cure time at 100°C. NH_2/NCO ratio: 1.0.

seems suitable for this purpose. The cure curve of the same sample (Fig. 6) is shown in Figure 7. Point A (Fig. 6) corresponds to the time (T_{90}) for torque to reach 90% of its value at 180 min. The DT is determined by a measurement of T_{90}.

The marked increase of E_B before DT may be ascribed not only to ordering of hard segments, but to increase of molecular weight, the latter being discussed below. Molecular weight is measured for each test piece (Fig. 6) and is plotted against cure time (Fig. 7). The molecular weight increases steadily with cure time to pass 4500 at 30 min and 6500 at 60 min when E_B begins to increase abruptly. The value of 4500 is exactly identical with rheological critical molecular weight (M_c) of PTMG.[10] A polymer of molecular weight higher than M_c shows intermolecular entanglement which works as pseudocrosslinks.[11] Thus, polyureaurethane at 60 min has a large enough molecular weight for entanglements to cause characteristic behavior of E_B after 60 min.

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