Aliphatic Polyureas: Melting Points versus Intrinsic Viscosities

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INTRODUCTION

Polyureas in the past have been prepared by means of different reactions. The use of several carbonic acid derivatives and substitution products, such as carbonic acid esters, phosgene, and carbon dioxide has been reported;[1,2] the use of carbon oxysulfide and diurethanes has also been studied.[3,4] The most commonly used reactants, however, are the diisocyanates.[5-12] As the number of methylene links between the polar groups in the polyureas is increased, the melting points decrease.[13,14]

On the other hand, ample evidence has been brought forward to show that, for a given type of polymer, the melting point increases with the molecular weight until the curve approaches asymptotically an upper limit which is at times referred to as the convergence temperature.[15-25]

Convergence Temperature Formulae. Garner et al.[15] developed the following formula for the convergence temperature T of normal long-chain hydrocarbons:

$$T = (0.6085n - 1.75)/(0.001491n + 0.00404) \quad (1)$$

where n is the number of carbons in the chain. Meyer and Wyk[26] proposed for these paraffins the relation

$$1/T = a + (b/n) \quad (2)$$

with $a = 2.395 \times 10^{-3}$ and $b = 17.1 \times 10^{-3}$ (T in °K.). They arrived at a convergence temperature of 145°C., i.e., 10°C. higher than given by the equation of Garner et al. Flory et al.[20,21] arrived at the correlation

$$(1/T) - (1/353) = 7.69 \times 10^{-4}/\bar{x}_n \quad (3)$$

where $\bar{x}_n$ is the number-average number of units per chain.

Melting points of some polyureas have been reported in the literature.[2,4,9,10,12]. These values

TABLE I
Melting Points of Aliphatic Polyureas as Reported in the Literature

Reaction components[a]		M.P., °C.	Inherent viscosity in *m*-cresol	Reference
1,6-Diaminohexane	+ CO$_2$	300	1.1	2
"	+ COS	300		4
"	+ HMDI	280-290		9
"	+ HMDI	270		10
"	+ HMDI	300		28
1,8-Diaminooctane	+ COS	260		4
"	+ TMDI	212-220		12
"	+ HMDI	220-225		9
1,9-Diaminononane	+ COS	215		4
1,10-Diaminodecane	+ CO$_2$	250	0.66	2
"	+ COS	220		4
"	+ COS	230		4
"	+ COS	237		27
"	+ COS	245		27
"	+ HMDI	210		9
"	+ DMDI	209-210	0.28	10
1,12-Diaminododecane	+ COS	205		4

[a] HMDI = hexamethylene diisocyanate; TMDI = tetramethylene diisocyanate; DMDI = decamethylene diisocyanate.

vary considerably within each species, as is shown in Table I.

EXPERIMENTAL

Reagents

Hexamethylenediisocyanate was obtained from an industrial source (Mobay Chemical Company, Pittsburgh, Pa.). The diamines were purchased (from Aldrich Chemical Company, Milwaukee, Wisc.) and then purified by high-vacuum distillation. The solid amines formed melt within 2°C. of the best literature melting points. The C, H, and N percentages were analyzed to be within 0.3% of calculated percentages. ACS grade acetone was used in all experiments.

Method of Polymerization

The amine was weighed in a dry nitrogen atmosphere and then dissolved in the acetone. The solution, 3 wt.-% of amine in 97 wt.-% of acetone was then charged to a 1000-ml. four-necked reaction flask which was equipped with a stirrer, gas-inlet tube, reflux condenser, and dropping funnel. The gas-inlet tube to introduce nitrogen led at the bottom of the flask into a glass-fritted gas dispenser. Depending on the reaction temperature employed, the reaction flask was either placed in a constant-temperature bath or equipped with an electric heating mantle. The hexamethylene diisocyanate was dissolved in acetone to form an 8 wt.-% solution which then was added through the dropping funnel to the agitated amine solution within 1/2 hr. Stirring was continued for another 1/2 hr., after which time the polymer dispersion was filtered through a Büchner funnel, using Whatman No. 2 filter paper. The polymer retained on the filter was washed with 200 ml. acetone three times and then with 200 ml. of absolute ether three times. The polymer was then dried in a dry nitrogen atmosphere for 3 hr. at 25°C. and in a vacuum oven for 24 hr. at 70°C. Then the viscosities were determined in a 0.3% phenol solution and the polymers redried for another 24 hr. If the viscosity values obtained after the second drying cycle were the same as those after the first cycle, which was true in most cases, these values were used. If not, the polymers were dried again for 24 hr. under the same conditions and further values obtained.

In order to establish whether any changes in melting point or intrinsic viscosity occurred after repeated drying cycles, two polymers were redried

for five consecutive 24-hr. periods. No significant changes could be measured after each period.

Intrinsic Viscosity Determination

The intrinsic viscosities were determined in phenolic solutions on the basis of the formula:

$$\eta = \left[\frac{\ln (t_x/t_0)}{c} \right]_{c \to 0}$$

where t_0 is the flow time of the solvent, t_x that of the solution, and c the concentration of the polymer. The viscosity values of solutions containing 0.1, 0.2, and 0.3 g./100 ml. phenol were extrapolated to zero in order to obtain the intrinsic viscosity. All viscosities were measured on fresh polymer solutions (within 2 hr. after preparation of the solution).

RESULTS AND DISCUSSION

The results of the intrinsic viscosity and melting point determinations are shown in Table II.

Figure 1 indicates that the melting points of the aliphatic polyureas exhibit a similar convergence behavior with increasing intrinsic viscosity to that which has been demonstrated in other polymers.[15−23,25,29,30] As should be expected, the melting points at convergence temperature decrease as the number of the carbon atoms between the urea groups increases. Those polyureas having an even number of carbon atoms have higher melting points than those containing the adjacent odd number of carbon atoms.
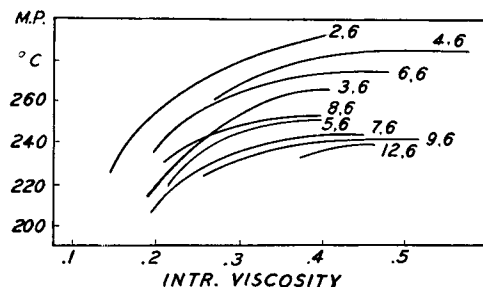

Fig. 1. Plots of melting point vs. intrinsic viscosity of polyureas (polymer designations as in Table II).

As is seen from Table I, the melting points of the 6,6-polyurea have been reported[2,4,9,10,28] in the literature to be 270, 280–290, and 300°C. In one case the melting point of 300°C. at an inherent viscosity of 1.1 in m-cresol is listed. This may be indicative that the curve of the 6,6-polymer in Figure 1 has not yet reached its asymptote.

<div style="text-align:center">TABLE II</div>

Urea polymer[a]	Reaction temp., °C.	Melting point, °C.	Intrinsic viscosity
2,6	+59	224	0.142
2,6	−20	263	0.223
2,6	−35	275	0.293
2,6	−50	293	0.402
3,6	+59	213	0.185
3,6	−20	245	0.275
3,6	−45	257	0.315
3,6	−65	266	0.404
4,6	+59	252	0.252
4,6	−10	280	0.32
4,6	−35	285	0.415
4,6	−55	283	0.610
5,6	59	209	0.205
5,6	0	239	0.268
5,6	−20	250	0.306
5,6	−35	251	0.394
6,6	59	234	0.192
6,6	0	260	0.248
6,6	−15	264	0.278
6,6	−45	274	0.475
7,6	59	205	0.190
7,6	0	235	0.264
7,6	−10	241	0.350
7,6	−25	243	0.440
8,6	59	232	0.210
8,6	0	248	0.300
8,6	−10	252	0.315
8,6	−25	253	0.392
9,6	59	224	0.250
9,6	20	239	0.392
9,6	−35	243	0.515
12,6	59	234	0.364
12,6	10	241	0.430
12,6	0	238	0.460

[a] The polymers are defined by the x, y values in the formula for the series: $-[NHCONH(CH_2)_xNHCONH-(CH_2)_y]_n$.

The intrinsic viscosity values reported in this work have been found to increase with the age of the polymer solution. Therefore, the measurements were taken within 2 hr. after the solutions were prepared. All polymers which were prepared by the method described precipitated in the reaction flask in the form of a fine powder which could easily be washed and dried.

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Synopsis

An homologous series of aliphatic polyureas of the type $[NH-CO-NH-(CH_2)_x-NH-CO-NH-(CH_2)_6]_n$ where the x = 2, 3, 4, 5, 6, 7, 8, 9, and 12, was prepared from

hexamethylene diisocyanate and diamines. The polymers were obtained in powder form with the use of acetone as the solvent. The intrinsic viscosities of the phenolic solutions of these polyureas were found to decrease with increasing polymerization temperature. When the melting points of the polymers were plotted against the intrinsic viscosities within each species of polymer, these melting points were found to increase with the intrinsic viscosity. The curves so formed appeared to approach an asymptote.

Résumé

Une série homologue de polyurées aliphatiques du type $+NH$—CO—NH—$(CH_2)_x$—NH—CO—NH—$(CH_2)_6+_n$ a été préparée à partir de diisocyanate d'hexaméthylène et de diamines. Les valeurs de x dans ces expériences sont 2, 3, 4, 5, 6, 7, 8, 9 et 12. Les polymères sont obtenus sous forme de poudre, le solvant employé étant l'acétone. On trouve que la viscosité intrinsèque de solutions phénoliques de ces polyurées diminue avec l'augmentation de la température de polymérisation. Lorsqu'on porte en diagramme les points de fusion des polymères en fonction des viscosités intrinsèques dans chaque espèce de polymère, on constate que les points de fusion augmentent avec la viscosité intrinsèque. Les courbes ainsi obtenues tendent vers une valeur asymptotique.

Zusammenfassung

Eine homologe Reihe von aliphatischen Polyharnstoffen des Typs $+NH$—CO—NH—$(CH_2)_x$—NH—CO—NH—$(CH_2)_6+_n$ wurde aus Hexamethylendiisocyanat und Diaminen hergestellt. Die x-Werte in diesen Versuchen waren 2, 3, 4, 5, 6, 7, 8, 9 und 12. Die Polymeren wurden in Pulverform erhalten, wobei Aceton als Lösungsmittel diente. Die Viskositätszahl der phenolischen Lösung dieser Polyharnstoffe nahm mit steigender Polymerisationstemperatur ab. Trug man innerhalb einer Polymergattung die Schmelzpunkte der Polymeren gegen die Viskositätszahlen auf, so fand man ein Ansteigen der Schmelzpunkte mit der Viskositätszahl. Die so erhaltenen Kurven scheinen sich einer Asymptote zu hähern.