Effect of Structure on the Glass Temperature
of Polyamides*

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Synopsis

A penetrometer method, for which validity was demonstrated, was utilized for measuring the glass temperatures of several polyamides. Adipic acid, sebacic acid, and hexamethylenediamine were used as representatives of linear aliphatic components of the nylons. Isophthalic acid, diphenic acid, and *m*-xylylenediamine were employed to provide examples with phenyl rings in the polymeric chain. Piperazine was used to assay the effect of a rigid alicyclic ring. To provide bulky side groups, 9,9-bis(2′-carboxyethyl)fluorene and 9,9-bis(3′-aminopropyl)fluorene were utilized. Several new nylon salts and polyamides were prepared. The results illustrate the contribution of chain stiffness and side chain bulkiness to the glass temperature, T_g. Assuming, as did Rybnikar, a T_g of $-65°C$. for nylon 66 and other linear aliphatic polyamides, the elevation caused by inclusion of a *m*-phenylene group in the chain was shown to be about 165°C. The piperazine ring had an effect at least equivalent to that of the *m*-phenylene group. A single bulky side group elevated the glass temperature by about 185°C. over the value for linear aliphatic polyamides, the same increment observed in the cases of polyesters and addition polymers. A second bulky group made a smaller incremental addition to T_g. Thus, a value of T_g well below room temperature for linear aliphatic polyamides was found consistent with the present results.

INTRODUCTION

In the work reported here, several polyamides were prepared containing rings incorporated in, or pendant to, the chain, and their glass transition temperatures T_g were determined by a simple penetrometer method. This permitted an assessment of the contribution of chain stiffness and bulkiness of the side chain to the T_g of polyamides.

EXPERIMENTAL

Chemicals

The diamines and dicarboxylic acids used in this work were all commercial chemicals with the exception of diphenic acid, 9,9-bis(2′-carboxyethyl)-fluorene, and 9,9-bis(3′-aminopropyl)fluorene. These latter chemicals were prepared during the course of other research in this laboratory.

Nylon Salts

Many of the salts (Table II) could be prepared in conventional fashion by mixing alcoholic solutions of diacid and diamine. However, some were quite soluble in alcoholic solution while others would not form in alcohols. (Thus a solution of diphenic acid and piperazine in methanol, after boiling for 1 hr., deposited only diphenic acid on cooling.)   The preferred procedure was to heat roughly equimolar amounts of acid and amine in distilled water (about 0.1 mole of salt/100 ml. of water) until solution was effected and then to adjust the pH of the resulting solution to about 7.2 by addition of either more diamine or more diacid.   The salt solution was then treated at 90–100°C. with charcoal for about 1 hr., filtered hot, and added to a large excess of isopropanol.   On cooling the salt usually precipitated.   If necessary, acetone was added to the water–isopropanol mixture to effect precipitation. The white salt was then recrystallized from methanol–isopropanol or water–isopropanol mixtures.

Polymerization

Salts derived from the relatively nonvolatile diamine, 9,9-bis(amino-propyl)fluorene, could be heated directly to effect polymerization to polyamides with $\eta_{sp}/c = 0.4$.   The other salts were sealed in evacuated tubes and heated to above the melting point of the salt (or at least 200°C.) for several hours.   The cooled tubes were opened and the prepolymers brought to higher molecular weight by heating at about 250°C. under nitrogen, first at atmospheric pressure and then at reduced pressure.

Polymer Sample Preparation

Upon completion of the polymerization cycle, the tubes were brought quickly to room temperature and the polymers removed.   Generally, a portion was used for the penetrometric test without further manipulation. Where a piece of polymer of the correct shape was not obtained, a sample, enclosed in aluminum foil, was flattened between the heated platens of a press.   If appreciable delay occurred before measurement could be made, the sample was kept in a stoppered vial, but no particular effort was made to dry it or keep it anhydrous.   The penetrometric T_g was the same for a freshly prepared polyamide or for a sample kept in a vial for over a year. All polymers tested, except the purchased nylon 66, were clear, glassy solids which gave no evidence of crystallinity by x-ray measurement.   A sample of nylon MXD-6, poly(m-xylylene adipamide), allowed to cool slowly after polymerization, crystallized to an opaque solid.   This sample gave no inflection in the temperature–penetration curve, i.e., the needle did not penetrate the sample between 25 and 150°C.   A sample of MXD-6 chilled after polymerization was obtained as a clear glassy solid and gave the T_g value reported here.

Molecular Weights

These were not determined as such. The reduced viscosity was measured as a 0.5% solution in 90:10 phenol–ethanol mixture at 25°C.

Measurement of T_g

The penetrometer was patterned after that of Edgar and Ellery.[1] A micrometer gage reading to 0.0001 in. was connected to a threaded fitting so that a disk of stainless steel could be attached. The disk was so made that a 6-in. stainless steel needle, 3 mm. in diameter, could be attached by a threaded fitting. (This provided for replacement of the disk by another of lighter weight, to give a total loading of 150 g. at the needle point, for melting measurements.[1] The total weight exerted at the needle point, which was 0.34 mm.^{2} in area, was 1000 g. Thus the initial loading on the polymer sample was 2.94 kg./mm.^{2} (1420 lb./in.^{2}). The apparatus was mounted on a heavy steel stand so that a heated bath of silicone oil could be raised
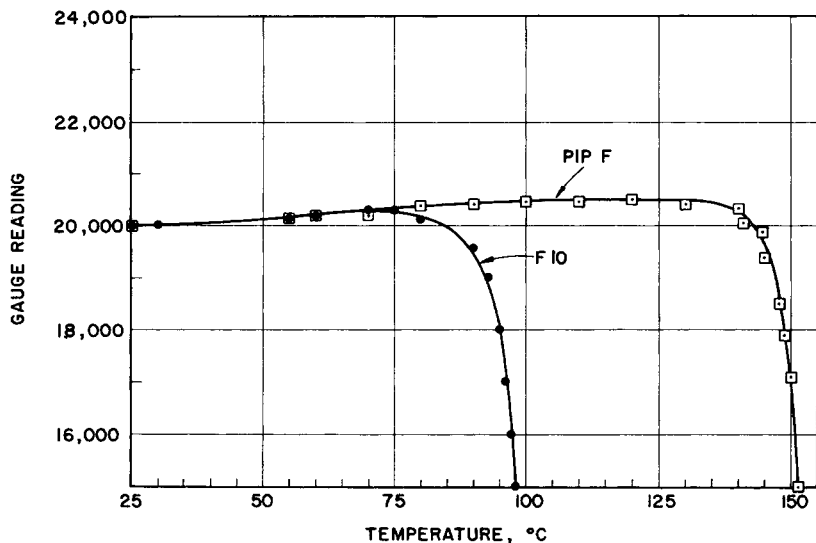

Fig. 1. Typical penetration–temperature curves for amorphous polyamides (load of 2.94 kg./mm.^{2}).

or lowered, by means of a laboratory jack, beneath the needle. A mechanically driven glass stirrer was placed in the bath. In practice the polymer sample was placed on a small glass stand in the oil and the needle brought to rest upon it. Heating and stirring were commenced and the gage readings and temperature of the bath simultaneously recorded. The rate of heating in the vicinity of the glass temperature was about 1°C./min. (based on approximate determination previously). T_g was determined by plotting the data and observing the point at which the curve suddenly changed in slope. Representative curves are shown in Figure 1. With
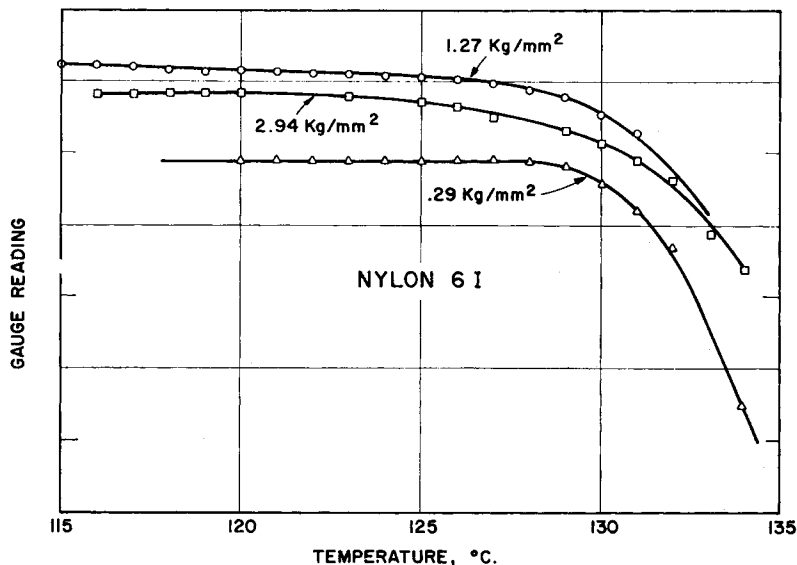
Fig. 2. Effect of load of penetration–temperature curve for nylon 6I.

nylon 66 samples the needle rapidly penetrated through to the glass support at room temperature.

Within the limits explored, the load had only a slight influence on the numerical values of penetrometric T_g for amorphous polyamides as illustrated in Figure 2. Thus when a needle point 0.785 mm.^{2} in area was used, corresponding to an initial load on the sample of 1.27 kg./mm.^{2} or approximately half that of the sharper needle, very similar values were obtained. With a loading of only 0.29/kg./mm.^{2} the T_g values obtained were, with a few selected samples tested, about 3–5°C. higher than those obtained with the heavier loadings (see Fig. 2). However, in practice the lightly loaded needle tended to stick and was not as convenient to use as the heavier loading. Moreover, with such a light loading the needle did not penetrate crystalline polymers, such as nylon 66, below the melting point.[1] The sharper needle, 2.94 kg./mm.^{2} load, with the use of which the data of Table II were obtained, clearly and rapidly distinguished linear aliphatic nylons from polyamides with T_g above 25°C. All references in what follows are to values obtained with this heavy (2.94 kg./mm.^{2}) loading.

PENETROMETER METHOD

The validity of the penetrometer for determining the glass temperature of polyesters was originally established by Edgar and Ellery.[1] The apparatus used in this work for determination of T_g was constructed after that of Edgar and Ellery[1] and differed basically only in the use of a sharper needle point (see Experimental Section). It therefore measures deformation of the polymer sample under greater stress than so-called heat distortion tests.[2]

TABLE I

Polymer	T_g, °C.[a]	Penetrometric T_g, °C.[b]
Polystyrene	95–100	94
Poly(methyl methacrylate)	72–105	91
Poly(vinyl chloride)	70–77	70
Poly(ethylene terephthalate)	67–81	69
Isopropylidenediphenol polycarbonate	145–150[c]	144

[a] Data of Holzmuller and Altenburg.[3]
[b] Determined in our laboratory.
[c] Data of Stille.[4]

Nevertheless, for a variety of amorphous polymers the values obtained by the penetrometer are very close to the values of T_g determined by a dilatometric method. The comparison, given in Table I, illustrates the validity of the penetrometric T_g.

Other workers have chosen to equate the penetrometric glass point with the brittle point.[5] The values obtained, however, were quite close to T_g values determined dilatometrically. Thus, Grieveson,[6] using an apparatus very similar to that employed in this work, determined the penetrometric brittle point T_b for a series of polyesters. He found that this T_b differed from the dilatometric glass temperature, T_g, being about 5°C. higher in most cases. Earlier, it had been found that the brittle point of a series of polymethacrylates agreed fairly well with T_g determined by other means.[7] Recently, Trick[8] has shown that a brittle point obtained from the data of the Gehman flex test[9] was consistently 15°C. higher than the dilatometric glass temperature for several elastomers.

A numerical difference of 5–15°C. is, in itself, of little meaning, since glass temperatures determined by methods of presumably equal reliance differ this much among themselves.[10] Thus, it can be held that the penetrometric glass temperature is a simple, useful, and rapid method of determining glass temperature or the point at which rapid segmental motion occurs in a polymer under normal use conditions.

The only previous use of the penetrometer for determination of T_g of polyamides was reported by Rybnikar.[11] He found values for nylon 6 and nylon 66 of about −65°C. which are considerably lower than the values usually reported for such polyamides. (Tyler and Whittaker[12] used the penetrometer for determining softening points of polyamides containing aromatic ether groups. Their results, however, clearly indicate that they have used the light loading which is better suited for determining melting points.)

RESULTS

Table II lists the diamine–diacid (nylon) salts not previously recorded in the literature as well as the glass temperatures, or inflections in the penetra-

tion–temperature curves, of the corresponding polyamides. With the exception of nylon 66 all polymers tested were amorphous and, in general, could not be easily crystallized.

TABLE II
Penetrometer Glass Temperature of Polyamides

No.	Diamine	Acid	Nylon salt[a] m.p., °C.[a]	Nylon designation	Polyamide	
					η_{sp}/c[b]	T_g, °C.[c]
1	Hexamethylene	Adipic	—	66[d]	1.63	<25
2	m-Xylylene	Adipic	—	MXD-6	0.84	73
3	Piperazine	Adipic	—	Pip-6	—	e
4	Fluorene dipropylamine[f]	Adipic	208	F6	0.84	120
5	Fluorene dipropylamine	Sebacic	215–219	F10	1.57	85
6	Hexamethylene	Diphenic	251	6D	0.40	127
7	m-Xylylene	Diphenic	209–210	MXD-D	0.15	159
8	Piperazine	Diphenic	136–137	Pip-D	0.10	193
9	Fluorene dipropylamine	Diphenic	163–167	FD	0.20	165
10	Hexamethylene	Isophthalic	227–228	6I	0.75	130
11	m-Xylylene	Isophthalic	233–234	MXD-I	0.53	165[g]
12	Piperazine	Isophthalic	252–253	Pip-I	0.20	192
13	Fluorene dipropylamine	Isophthalic	h	FI	0.68	175
14	Hexamethylene	Fluorene dipropionic[i]	220–222	6F	0.44	122
15	m-Xylylene	Fluorene dipropionic	185–186	MXD-F	0.40	150
16	Piperazine	Fluorene dipropionic	100–102	Pip-F	0.16	145
17	Fluorene dipropylamine	Fluorene dipropionic	212–214	FF	0.59	165

[a] Values given for salts not previously reported.
[b] For 0.5% solution in 90:10 phenol–ethanol at 25°C.
[c] Beginning of inflection point of curve.
[d] Commercial sample, Zytels 211 and 42 behaved similarly.
[e] No T_g value; polymer could not be obtained in amorphous form.
[f] 9,9-Bis(3′-aminopropyl)fluorene.
[g] Lum and Carlston[16] report a "softening point" of about 150–170°C.
[h] Hygroscopic, not measured.
[i] 9,9-Bis(2′-carboxyethyl)fluorene.

Adipic acid, sebacic acid, and hexamethylenediamine were used as representatives of linear aliphatic components of the nylons. Isophthalic acid, diphenic acid, and m-xylylenediamine were employed to provide examples with phenyl rings in the polymeric chain. Piperazine was used to assay the effect of a rigid alicyclic ring in the chain. To provide bulky side groups, 9,9-bis(3-aminopropyl)fluorene and 9,9-bis(2-carboxethyl)fluorene were utilized.

The effect of molecular weight is illustrated by results with nylon 6D. Polymers with $\eta_{sp}/C = 0.12$ exhibited a T_g of 118°C. (two separate preparations) in comparison with the value of 127°C. for a polymer with $\eta_{sp}/C = 0.40$. This result is in line with previously reported [6,7,13-15] examples of the effect of molecular weight on glass temperature. This effect must be considered with reference to the data of Table II and about 10°C. added to the T_g values of Nos. 7, 8, and 16 to make them comparable with the others.

The data of Table II show conclusively that the incorporation of phenyl rings in the chain causes appreciable elevation of the glass temperature. Where both the acid and amine components of the polyamide (Table II, Nos. 7 and 11) contain phenyl groups, T_g is raised to the neighborhood of 160–165°C. A comparison of the polyamides where piperazine was substituted for m-xylylenediamine shows that the rigid heterocyclic ring contributes at least as much to T_g as a m-phenylene linkage and probably more. The F-polyamides, those containing the fluorene nucleus, demonstrate that a sufficiently bulky side group makes a contribution to T_g equivalent to that of a phenylene linkage.

DISCUSSION

The literature[17-21] reports a series of determinations of T_g for linear aliphatic nylons ranging from 24 to 49°C. In our hands the penetrometer needle rapidly cut through nylon 6 or nylon 66 at room temperature. This is more nearly in accord with the results of Rybnikar,[11] who found T_g for these polyamides to be −65°C. when using a penetrometer with essentially the same loading as used in this work. (A lightly-loaded needle does not penetrate these nylons at room temperature.)

The detection of a transition in aliphatic nylons between 45 and 90°C., by thermal expansion, dynamic mechanical, and thermogravimetric methods, obviously reflects the onset of some sort of molecular motion in the polymer. It should be noted, however, that a careful study of nylon 66[22] showed no heats of transition could be detected in the neighborhood of 47°C. Further, Kawaguchi[23] found, in agreement with Woodward,[24] that linear aliphatic polyamides exhibit a β-dispersion (dynamic modulus method) at about −40°C. Moreover, as Rybnikar points out, the ease of crystallization of linear aliphatic nylons at well below room temperature[25] indicates strongly that the glass transition, or what is usually conveyed by that expression, is indeed well below room temperature. The penetrometric behavior of these aliphatic linear polyamides, rapid penetration at room temperature, is distinctly different from that of the other polyamides which show well defined T_g values above room temperature.

In support of the low T_g value for aliphatic nylons, the reported value of −58°C.[26] for a linear aliphatic polyurethane, which is also capable of hydrogen bonding, may be cited.

The results reported in this paper were not influenced by crystallinity. All of the polymers listed in Table II, except nylons 66 and Pip-6, were in an amorphous condition when tested. Most crystalline polymers do not show

an inflection in the penetration–temperature curve below the melting point.[1] Thus we were unable to obtain a T_g value for a crystallized sample of poly-(m-xylylene adipamide) (MXD-6). The value given in Table II was obtained on a quenched, amorphous sample. This behavior is in striking contrast to that of nylon 6 and nylon 66 which, although partially crystalline, permitted rapid and deep penetration by the needle at room temperature.

It is worthy of comment that polyamides are, in general, not necessarily brittle below T_g, in distinct contrast to many polymers and the generalized descriptions[27–29] of glass temperature found in the literature. The important criterion in determining toughness, or impact resistance, of the amorphous polyamides with high T_g is molecular weight. For example, the F-polyamides (F6, 6F, FI, MXD-F, and FF), all with T_g above 120°C., were brittle when η_{sp}/C was below about 0.4 but became quite tough, giving Izod notched impact values in excess of 1.0 ft.-lb./in. at room temperature, when the molecular weight increased. Seemingly, the toughness of polyamides is not related to their being above or below T_g although severe cooling, say to below −80°C., renders them brittle.

The effect of phenylene linkages, particularly *para* links, on the melting point of crystalline polymers has been well documented.[30,31] Less information is available about the effect of phenylene linkages in the chain on the glass temperature. Numerous references[32–36] describe "softening points" of polyamides with o-, m-, and p-phenylene linkages. In most of these instances the method of measurement is not defined and is not necessarily related to T_g. Nevertheless, the data of Conix[37] for polyanhydrides and Eareckson[38] and Conix[39] for polyesters have shown that phenyl rings in condensation polymers have a pronounced elevating effect on T_g. The results presented here confirm this generalization for polyamides. A value of 123°C. was reported for poly(heptamethylene terephthalamide), nylon 7T,[19] which corresponds fairly well to the values found in this work for nylons 6D and 6I which, like nylon 7T, contain one phenylene group per repeat unit in the polymer chain. The increment in T_g for the nylons containing an aromatic ring over a linear aliphatic nylon, assuming a value of −65°C. for nylon 66, is then about 160°C. Similarly, poly(ethylene terephthalate) shows an increment in T_g over poly(ethylene adipate), which has a T_g of −70°C.,[30] of about 140°C.

Again, a value of −65°C. for linear aliphatic nylons is reasonable if one compares poly(m-xylene isophthalate) with poly(m-xylylene isophthalamide) (MXD-I), which differs only in the polar linkage. The T_g of the polyester, 143°C. (as determined by the penetrometer method in our laboratory). is a little lower than the T_g (165°C.) of the polyamide. Thus a polyamide containing phenylene linkages derived from both the acid and amine components has a T_g value approximately 230°C. higher than a linear aliphatic polyamide, while a polyester containing phenylene linkages from acid and alcohol components shows a T_g elevation of about 215°C. over the linear aliphatic polyester.

The stiff piperazine ring, in replacing a chain of methylenes, causes an increase in glass temperature at least equivalent to that of a m-phenylene ring.

The effect of bulky side chains in increasing glass temperatures of addition polymers has been observed.[27,29b] For example, if T_g for polyethylene is taken as $-125°C.$,[8] then the contribution of a side chain phenyl group (as in polystyrene) is at least 200°C. in a positive sense. Tobolsky[40] considers $-81°C.$ as a more realistic value of T_g for polyethylene; thus the incremental effect of the phenyl group may be about 180°C. The increase of T_g in polyamides by the addition of a bulky side chain, from our results, is also quite large. One fluorene nucleus as a side chain (see Table II), causes an increase of about 185°C. if one uses Rybnikar's T_g value for nylon 66.

An inspection of the data of Table II reveals that a second bulky group does not have the same quantitative effect as the first. Thus, nylons F6 and 6F, with one bulky group per polymer repeat unit, have glass temperatures about 185°C. higher than nylon 66, while nylon FF, with two bulky groups per repeat unit, has a T_g only 20–25°C. additionally higher. The same is true with rigid groups in the backbone chain. Replacing adipic acid in nylon 66 with diphenic or isophthalic acids causes an increase in T_g of about 165°C., but nylons MXD-D or MXD-I, with at least twice the density of phenylene linkages, show an additional increase in T_g of only about 35°C. over nylon 6D or 6I.

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Résumé

On a employé une méthode pénétrométrique, dont la validité a été démontrée, pour mesurer la température de transition vitreuse de plusieurs polyamides. On a employé l'acide adipique, l'acide sébacique et l'hexaméthylène diamine comme représentants de composants linéaires aliphatiques des nylons. On a employé l'acide isophtalique, l'acide diphénique et la *m*-xylylène diamine pour fournir des exemples dans lesquels les noyaux phényles sont présents dans la chaîne polymérique. On a employé la pipérazine afin de tester l'effet d'un noyau alicyclique rigide. Afin de montrer l'influence des groupes latéraux volumineux, on a employé le 9,9-bis(2'-carboxyéthyle) fluorène et le 9,9-bis(3'-aminopropyl)fluorène. On a préparé plusieurs nouveaux sels de nylon et polyamides. Les résultats illustrent la contribution de la rigidité de la chaîne et des groupes volumineux latéraux de la chaîne sur la température de transition vitreuse T_g. En admettant suivant Rybnikar un T_g de $-65°C$ pour le nylon 66 et autres polyamides aliphatiques linéaires, on a montré que l'élévation de température causée par l'inclusion d'un groupe *m*-phénylène dans la chaîne était d'environ 165°C. Le cycle pipérazine a un effet au moins équivalent à celui d'un groupe *m*-phénylène. Un simple groupe volumineux latéral élève la température de transition vitreuse d'environ 185°C au-dessus de la valeur correspondant aux polyamides aliphatiques linéaires, le même incrément que celui observé dans le cas des polyesters et polymères d'addition. Un second groupe plus volumineux donne une plus petite augmentation de l'incrément à T_g. Une valeur de T_g bien inférieure à la température de chambre pour des polyamides linéaires aliphatiques, correspond donc à, ces résultats actuels.

Zusammenfassung

Eine Penetrometermethode, deren Brauchbarkeit gezeigt wurde, wurde zur Messung der Glastemperatur einiger Polyamide herangezogen. Als Vertreter linearer aliphatischer Komponenten von Nylon wurde Adipinsäure, Sebacinsäure und Hexamethylendiamin verwendet. Zur Darstellung von Proben mit Phenylringen in der Polymerkette wurde Isophthalsäure, Diphensäure und *m*-Xylylendiamin herangezogen. Als Komponente

mit einem starren alizyklischen Ring wurde Piperazin verwendet. Seitengruppen mit starker Raumbeanspruchung wurden mit 9,9-Bis-(2'-carboxyäthyl)fluoren und 9,9-Bis(3'-aminopropyl)fluoren erhalten. Einige neue Nylonsalze und Polyamide wurden dargestellt. Die Ergebnisse zeigen den Beitrag der Kettensteifigkeit und der Raumbeanspruchung der Seitenkette zur Glastemperatur T_g. Unter der Annahme einer T_g von −65°C für Nylon 66 und andere lineare aliphatische Polyamide, in Übereinstimmung mit Rybnikar, ergibt sich die durch Einschluss einer m-Phenylengruppe an die Kette verursachte Erhöhung zu etwa 165°C. Der Einfluss des Piperazinringes war demjenigen der m-Phenylengruppe zumindest gleichwertig. Eine einzelne Seitengruppe mit hoher Raumbeanspruchung erhöht die Glastemperatur um etwa 185°C über den Wert für lineare aliphatische Polymere; das gleiche Inkrement wurde im Falle von Polyestern und Additionspolymeren beobachtet. Eine zweite Gruppe mit grosser Raumbeanspruchung lieferte ein kleineres Erhöhungsinkrement zu T_g. In Übereinstimmung mit den vorliegenden Ergebnissen wurde ein T_g-Wert weit unterhalb Raumtemperatur für lineare aliphatische Polyamide gefunden.