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Metalation and N-Alkylation of some Polyamides

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Dedicated to Prof. Dr. Dragutin Fleš on the occasion of his 60th birthday

Summary

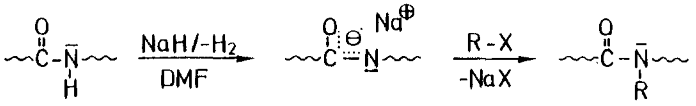
Totally N-substituted polyamides were synthesized starting from poly(2,4,4-trimethylhexamethylene terephthalamide) by metalation of the amide groups and subsequent reaction with several electrophiles. Polyamides of this structure are not available from terephthalic acid and the corresponding diamines by polycondensation. This N-alkylation reaction can be used for the synthesis of comb-like graft copolymers. The solubilitity and the thermal properties of these polyamide derivatives are described.

Introduction

Polyamides can be chemically modified at the amide groups as well as at the carbon atoms. Radical reactions leading to substitution at the C-atoms have been described elsewhere1), and are mostly used for the synthesis of graft copolymers. In exceptional cases, the carbon atoms could be selectively attacked using special initiator systems2) but in general random attack is observed. Selective modification of the amide groups has also been examined3). Thus, for example, N-hydroxymethylated or N-grafted polyamides could be produced by the reaction of polyamides with formaldehyde and epoxides, respectively. The conversion of polyamides with hypochlorites, trifluoroacetic acid and other anhydrides led to polyamide derivatives which, inter alia, could be used as polymer reagents[4]. A selective, radical N-grafting is possible starting from N-chloropolyamides[5]. Some other graft reactions and partial substitutions at amide nitrogen via metalation of the amide groups of some polyamides with sodium in liquid ammonia were recently described[6]. A remarkable decomposition of the polyamide backbone under the strong metalation conditions was however also found. In the following it will be shown that metalation can be carried out under alternative conditions and that a large number of N-substituted polyamides may be prepared in that manner.

Results and Discussion

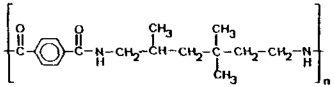
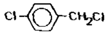
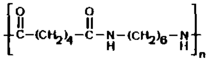
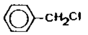
Polyamide anions are formed by the reaction of polyamides with sodium hydride in N,N-dimethylformamide (DMF). N-substituted polyamides are obtained after addition of such electrophiles as are stable to sodium hydride (see Eq.1).



$$\sim\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\bar{N}}}\sim \xrightarrow[DMF]{NaH/-H_2} \sim\overset{O}{\overset{\vdots\ominus}{C}}\overset{Na^{\oplus}}{\cdots}\underline{N}\sim \xrightarrow[-NaX]{R-X} \sim\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{\bar{N}}}\sim \qquad (1)$$

This reaction was carried out with two commercial grade polyamides: Ultramid A3® (polyamide 66, BASF AG) and Trogamid T® (TT, poly(2,4,4-trimethylhexamethylene terephthalamide, DYNAMIT NOBEL AG)(see Table 1). The following investigations are concentrated on Trogamid T®. In the caseof N-B-TT (for abbreviations see Table 1) the conversion (in terms of DS) was determined by chlorine analysis following the method of Schöniger[7]. In the other cases the conversion was determined by NMR measurements. As an example Fig.1 shows the NMR spectrum of N-C_{11}-TT. It exhibits three peaks in the ratio $H_a : H_b : H_c = 1 : 2 : 14$ indicating a complete substitution. This result is supported by the fact that

TABLE 1 : N-Alkylation of Polyamides according Eq. 1

Polyamide	RX	DS/% *)	Product (Abbreviation)
 Trogamid T ® (TT)		14,70,100	N-B-TT
		100	N-C_6-TT
		100	N-C_{11}-TT
		100	N-A-TT
		100	N-U-TT
 Polyamide 66		5 - 65	

*) degree of substitution / percent of substituted amide groups

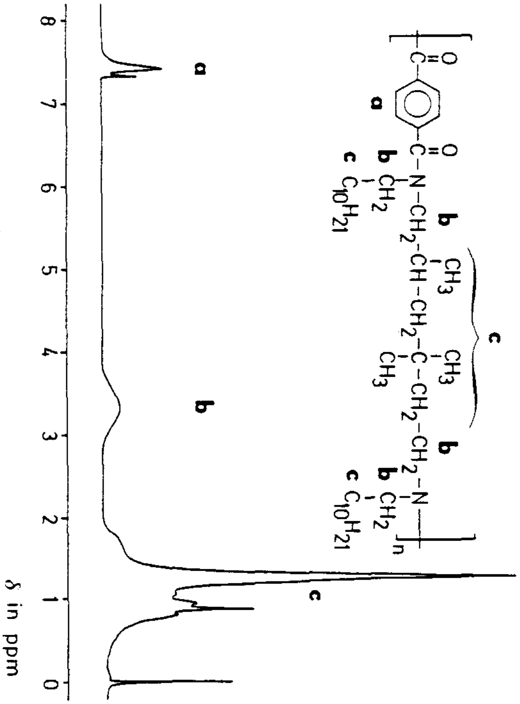


Figure 1 : 90 MHz ^{1}H-NMR spectrum of N-C_{11}-TT in $CDCl_3$

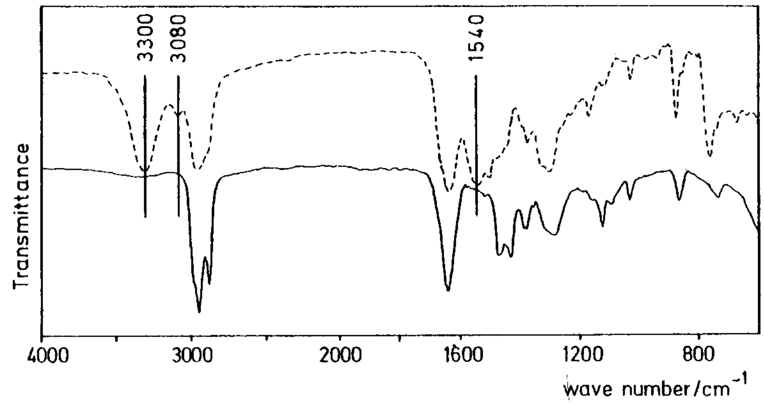


Figure 2: IR spectra of TT (---, film from $CHCl_3$/MeOH (4:1)) and N-C_{11}-TT (—, film from $CHCl_3$)

the proton resonance of unsubstituted amide groups is absent. Moreover, a complete substitution is consistent with the lack of the N-H absorption (at 3300 and 3080 cm^{-1}) and the amide-II-band (at 1540 cm^{-1})in the IR spectra (see Fig.2).

By modification of the reaction conditions the degree of substitution (DS) can be varied over a wide range. Under the conditions described in the experimental section all amide groups are substituted. Thus chemically uniform polyamides unavailable from terephthalic acid and the corresponding diamines by polycondensation [8] can be synthesized. Polyamides containing long aliphatic chains at the amide groups (e.g. N-C_{11}-TT, N-U-TT) represent new comb-like polymers. In two cases (N-A-TT, N-U-TT) a reactive substituent containing a double-bond was introduced. The latter polymers can be further modified. Reactions according to Eq.(1) with n-butyllithium or phenyllithium instead of sodium hydride did not lead to N-substituted polyamides. Presumably the lithiated amide groups are not sufficiently nucleophilic to carry out the second step of the reaction.

The N-substitution has a strong influence on the properties of polyamides. TT itself is soluble in polar solvents such as formic acid, sulfuric acid, hexafluoroisopropanole, dimethylsulfoxide and N,N-dimethylformamide but insoluble in less polar solvents such as tetrahydrofurane, dioxane, chloroform or dichloromethane. While N-B-TT with a DS of 14% shows the same solubility properties as TT, N-B-TT with a DS of 70% and the other substituted TT derivatives are soluble in the less polar solvents mentioned above. The absence of hydrogen bonding could be invoked to explain this behaviour.

The thermal behaviour of the N-substituted polyamides was examined by differential thermal analysis (DTA). It was found that the glass transition point (T_g)sinks continuously with increasing degree of substitution.This is illustrated in Fig.3. An increasing degree of substitution involves a diminishing extent of hydrogen bonds and this effects a rise of the chain flexibility in the melted state. This leads to a larger gain in entropy on passing from the glass-like state into the melt, and this in turn causes a decreasing glass transition point[9]. On the other hand the chain flexibility in the melted state is reduced by an increasing steric hindrance caused by the substituents. However, the latter effect is of secondary importance.

The glass transition points decrease with increasing length of the side chain. This is illustrated in Fig.4 for totally alkylated TT derivatives. On account of their great flexibility the side chains act as plasticizer. They enwrap each single polymer chain and screen the polar amide groups. This effect of internal softening, leading to an increased chain flexibility in the melted state, increases with the length of the side chains.

N-C_{11}-TT (T_g = -22°C) and N-U-TT (T_g = -21°C) have almost identical glass transition temperatures. This indicates that at least in the case of long side chains the double bond has no significant effect on the thermal properties.

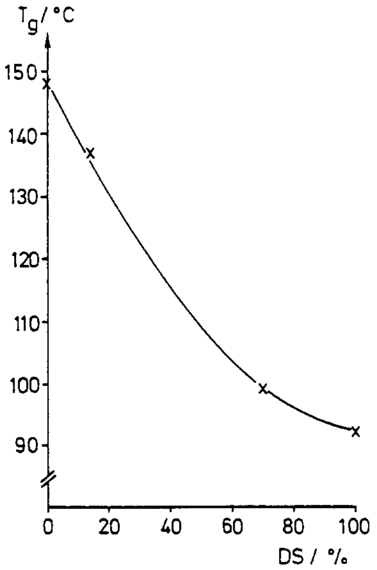


Figure 3 : Glass transition temperature (T_g) of N-B-TT as a function of the degree of substitution (DS)

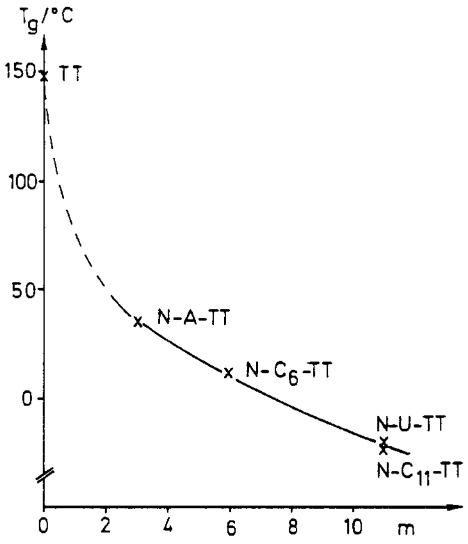


Figure 4: Glass transition temperature (T_g) of N-substituted TT derivatives as a function of the number of C-atoms (m) of the substituent

Experimental

Preparation of totally N-substituted TT derivatives: At room temperature 3,0 g of dry Trogamid T® were dissolved under stirring in 150 ml of DMF and then metalated by the addition of 0.11 mole of sodium hydride (3,2 g, 80% suspension in paraffin). After 24 hours 0,04 mole of RX were added and the reaction mixture was stirred for another 24 hours. The excess of sodium hydride was destroyed by addition of 300 ml of water under cooling. By this the N-substituted polyamide precipitated. The precipitate was filtered off, washed with water till neutral, dissolved in chloroform and washed with water. The excess RX was separated on reprecipitation with methanol (N-C_6-TT: petrol ether). N-B-TT and N-A-TT were dried in a vacuum desiccator over P_2O_5. The other products were freeze-dried from benzene.

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