

## **Anisotropic polyaramide/polyol dispersions – new components for the preparation of polyurethane microcomposites**

**Susanne Demharter, Joachim Rösch\*, and Rolf Mülhaupt**

Freiburger Materialforschungszentrum and Institut für Makromolekulare Chemie der Albert-Ludwigs Universität, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany

### **Summary**

Polymerization of N-(p-aminobenzoyl)-caprolactam (PAC) in melts of polyols such as dihydroxy-terminated oligo(oxytetramethylene) with  $M_n=2000$  g/mol at 200°C afforded stable dispersions of poly(p-phenylenebenzamide) whiskers in polyol. In spite of the low molecular weight of the polyaramide, which was isolated by solvent extraction, the microparticles are efficient reinforcing agents of polyurethanes because of the excellent interfacial adhesion resulting from covalent attachment of the polyols onto the microparticle surfaces. The role of the competing formation of p-aminobenzoate-terminated polyols via esterification of PAC was investigated. Morphological and mechanical properties of polyurethane microcomposites, prepared from poly(p-phenylenebenzamide)/poly(oxytetramethylene)diol dispersions and 4,4'-diisocyanatodiphenylmethane, were determined as a function of the microparticle content. When compared to conventional polyurethanes, containing equivalent amounts of spherical organic and inorganic fillers, the microcomposites give higher Young's modulus, tensile strength without sacrificing high elongation at break.

### **Introduction**

Since the early pioneering advances of Otto Bayer (1), polyurethanes, prepared by stepgrowth polymerization of polyols with polyfunctional isocyanates, are well established as versatile materials with a wide range of applications, e.g., foams, elastomers, thermoplastics, coatings, fibers, and adhesives. Polyurethane properties are tailored to meet the highly diversified product requirements by varying the polyurethane microstructures or by dispersing inorganic or organic fillers into the polyurethane matrix (2). Fillers play an important role in polyurethane formulation to improve the stiffness/strength/toughness balance. Frequently, modulus and stiffness are enhanced at the expense of toughness. One successful approach to overcome this toughness/stiffness limitation has been to use dispersions of polymeric microparticles in polyols, referred to as polymer polyols (3,4). For instance, acrylonitrile or styrene/acrylonitrile is polymerized in the presence of polyetherpolyols to form dispersions which are stabilized by in-situ formation of polyetherpolyol graft copolymers as polymeric dispersing agents (5). Alternatively, stepgrowth polymerization of diamines with polyfunctional isocyanates produces phase-separated polyurea micro-

\*Corresponding author

particles which are dispersed in the polyol. Here the in-situ dispersing agents consist of polyurea-block-polyol di- or multiblock copolymers (6). Most of the polymer polyols contain 20-30 wt.-% of dispersed isotropic microparticles with average diameters in the range of 1000 nm.

In the case of fiber- as well as filler-reinforced polymeric systems (7), it is well known that anisotropic slab-like or needle-shaped microparticles give substantially higher modulus and strength. In such multiphase polymer systems the reinforcement depends upon the volume fraction and the aspect ratio, i.e., the ratio of length to diameter, of the dispersed rigid anisotropic microphases (8). In a previous communication (9) we have reported the in-situ polyamide microcomposite formation via polymerization of N-(p-aminobenzoyl)-caprolactam in polyamide-6 melts. Here we describe the polymerization of N-(p-aminobenzoyl)-caprolactam in polyol melts. Objective has been to prepare polymer/polyol dispersions containing anisotropic poly(p-phenylene bezamide) microparticles and to investigate the possibility of utilizing such dispersions as components for the synthesis of polyurethane microcomposites.

## Experimental

**Materials:** The N-(p-aminobenzoyl)-caprolactam was prepared from p-aminobenzoic acid via the p-sulfinylaminobenzoyl chloride as described by Mathias, Moore and Smith (10). The crude product was recrystallized twice from ethylacetate and melts at 153° C. Diol-terminated poly(oxytetramethylene) (PTF),  $M_n=2000$  g/mol, was supplied by BASF AG/Ludwigshafen. The 4,4'-diisocyanatodiphenyl-methane (Baymidur K88, NCO-equivalent 130-140) was obtained from Bayer AG/Leverkusen. The p-aminobenzoic-acid terminated poly(oxytetramethylene) (PTHF-PAB) was prepared by esterifying 120 g (0,06 mol) of the diol-terminated poly(oxytetramethylene) with 24 g (0,14 mole) p-aminobenzoic-acid-ethylester in the presence of 0,14 g (0,1 wt.-%) dibutyltindilaurate. The reaction temperature was increased during 24 h from 180°C to 220 °C and residual ethanol and ethyl(p-aminobenzoate) were distilled off under  $10^{-3}$  bar vacuum. The degree of esterification was 96%, as determined by titration of the amine-groups. For comparison polymer/polyol dispersions were prepared by polymerization of acrylonitrile in PTHF. Typically a solution of 0,27 g AIBN in 11 g acrylonitrile is added dropwise during 1 h to 100 g PTHF at 75 °C under nitrogen atmosphere. After 30 min the PTHF reaction mixture turns opaque and the polymerization is continued for 6 h at 80 °C. Afterwards non-reacted acrylonitrile is stripped off under vacuum ( $10^{-2}$  bar) and the resulting dispersion contains 10 wt.-% of dispersed polyacrylonitrile particles. Glass beads coated with 0,2 wt.-% aminopropylsilane (G5000 CP0320) were obtained from Potters Ballotini.

**Polymer/polyol synthesis:** The polymerization of N-(p-aminobenzoyl)-caprolactam (PAC) in diol-terminated poly(oxytetramethylene) was performed in a dry 250 ml three-necked round-bottom flask equipped with stirrer, nitrogen inlet and a Liebig condenser. In a typical run, 25g of PTHF diol with  $M_n=2000$  g/mol was heated to 200 °C. Then 2.5 g PAC was added to form a clear solution. After 15 minutes the clear solution turned opaque and the solution viscosity started to increase. In the

preferred process stirring is suspended during particle formation. The temperature was raised to 240 °C and during 30 minutes the caprolactam was distilled off under oil-pump vacuum ( $10^{-2}$  bar). Brookfield viscosity of the neat PTHF was  $1,4 \cdot 10^{-3}$  cps while that of the polyamide-dispersion was  $20 \cdot 10^{-3}$  cps at 1 rpm and 40 °C. In order to obtain polymer polyols containing lower polyamide content, this dispersion was diluted with additional PTHF.

**Polyurethane microcomposites:** Polyurethanes were prepared from poly(p-phenylene-benzamide)/PTHF and 4,4-diisocyanatodiphenyl-methane without adding chain extenders. In a typical run, the dispersions described above were dried at 50 °C and  $10^{-2}$  bar for the duration of 2h. Then 4,4'-diisocyanatodiphenyl-methane (Baymidur K88) was added at a NCO/OH molar ratio of 1.05 mol/1.00 mol to ensure chain extension and weak crosslinking via allophanate formation. The resulting mixture was poured into a mold consisting of two glass plates separated by a rubber sealing of 2 mm thickness. Curing was performed 3 hours at 100 °C.

For stress/strain measurements dumbbell-shaped tensile bars were cut as described by DIN 53504 standards. Young's modulus, tensile strength and elongation at break were determined from stress/strain curves recorded on an Instron 4204 at 23 °C and 100 mm/min crosshead speed. At 400% elongation, repeated cyclic stress/strain experiments were carried out to examine the elastomeric nature of the polyurethane samples. Morphological studies were performed using the Leitz Pol BK polarized light microscope and the Zeiss DSM 960 scanning electron microscope (SEM) at 15 kV. For polarized light microscopy a thin layer of the polymer-polyol dispersions was kept between glass slides. For the scanning electron microscopic investigation the polymer-polyol dispersions were sprayed onto an aluminum support which was subsequently sputtered with gold.

Solid-state MAS  $^{13}\text{C}$ -NMR was recorded using a Bruker CXP 300 at 75,47 MHz. Amine-endgroup titration with 0,1 n  $\text{HClO}_4$  in glacial acetic acid/THF 1:1 was performed on a Mettler DL 25 titrator. Brookfield viscosities were recorded using a Brookfield Digital Viscosimeter Model DV 2 with spindle No. 21 at 40 °C.

## Results and discussion

When N-(p-aminobenzoyl)-caprolactam, referred to as PAC, is added to the melt of poly(oxytetramethylene)diol of  $M_n=2000$  g/mol, referred to as PTHF, at temperatures between 200 and 240 °C, the PAC is consumed within few minutes. At 10 wt.-% PAC content, dispersions are obtained, whereas at lower PAC concentrations the reaction mixture remains homogeneous. Shown in Figure 1 are SEM images of the resulting polymer polyols which contain needle-shaped microparticles of approximately 1000 nm length. These microparticles retain their dimensional stabilities when exposed to 200 °C over prolonged periods of time. Similar whiskers have been observed in the case of in-situ polyamide microcomposites when PAC is polymerized in polyamide-6 melts (9).

In principle, there exist three feasible reaction pathways for the reaction of PAC in PTHF melts. As illustrated in Scheme 1, PAC polymerization can occur via the ring-opening pathway or the elimination pathway.

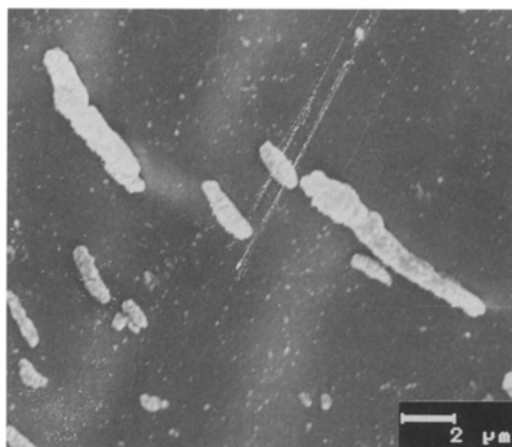
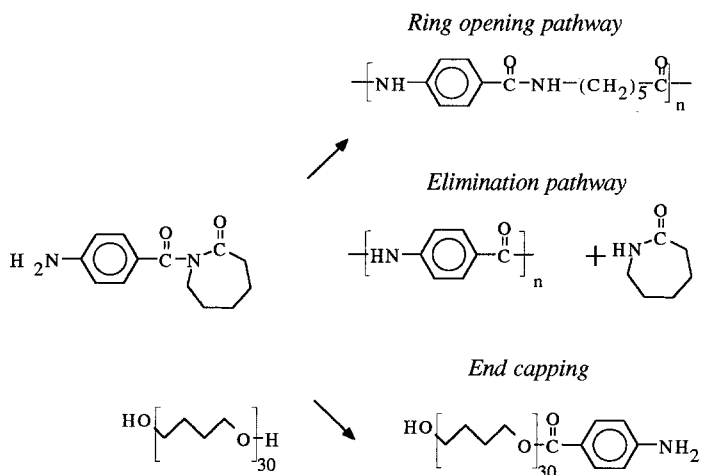


Figure 1. SEM-observation of anisotropic polymer particles obtained by in-situ polymerization of 10 wt.-% PAC in PTHF at 200 °C.

In the elimination pathway, caprolactam is eliminated when the amine attacks at the exocyclic carbonyl group. This pathway leads to the desired rigid poly(p-phenylene benzamide). Endocyclic attack of the amine at the carbonyl group of the lactam ring, however, yields the more flexible alternating copolymer of p-aminobenzoic acid and 6-aminocaproic acid, which possess considerably lower modulus with respect to the poly(p-phenylene benzamide). When ring opening and caprolactam elimination take place at the same time, the resulting polyamide contains both 6-aminocaproic acid and p-aminobenzoic acid structural units.



Scheme 1. Reaction pathways for the thermal polymerisation of PAC

According to Smith et al. (10) and Walsh et al. (11), contributions of the two reaction pathways are strongly dependent upon the polymerization temperature. At temperatures  $<200\text{ }^{\circ}\text{C}$ , the elimination pathway is favored, while at temperatures  $>200\text{ }^{\circ}\text{C}$  the ring-opening pathway accounts for the incorporation of 6-aminocaproic acid units into the rigid poly(p-phenylene benzamide) backbone. In the presence of the PTHF-hydroxy endgroups, a third pathway must be taken into account. Since the PAC represents an activated derivative of p-aminobenzoic acid, also attack of the hydroxy groups can occur at the exocyclic carbonyl group, thus eliminating caprolactam and esterifying PTHF with p-aminobenzoic acid. This third reaction pathway in Scheme 1 depends upon the OH/PAC molar ratios. At high OH concentration or low PAC content respectively, the esterification reaction represents an important side reaction which consumes PAC. Therefore, both PAC concentration and reaction temperature are important parameters governing the formation of polymer polyol dispersions.

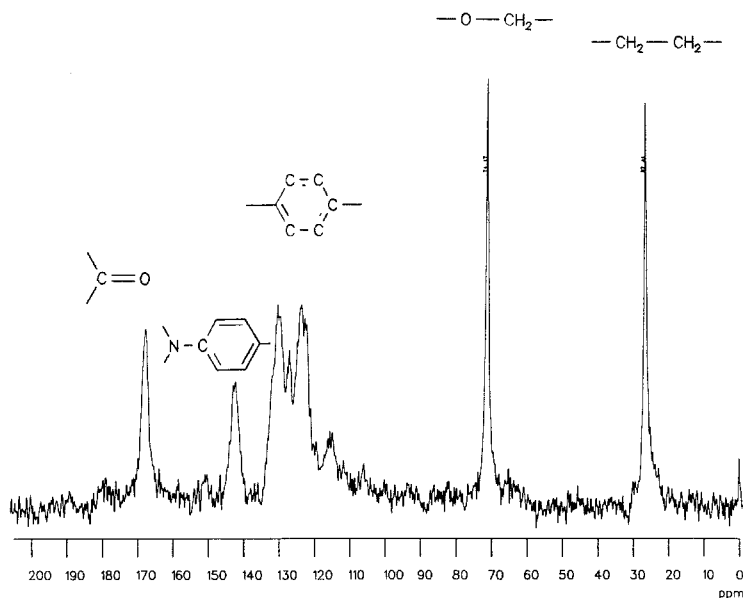


Figure 2. 75.47 MHz MAS-<sup>13</sup>C-NMR of PAC polymerized in PTHF

When the amount of the eliminated caprolactam is measured as a function of the polymerization temperature, 95 % of the theoretical amount are recovered after few minutes at 200 and 230 °C. This indicates that PAC reactions are very rapid. As another consequence, elimination and end-capping pathways appear to be much more important with respect to the ring-opening polymerization. In fact, as apparent from Figure 1, the 75,47 MHz MAS-<sup>13</sup>C-NMR spectroscopic investigation of the dispersed microparticles, which were purified by extracting the dispersion with acetone

and by recovering the particles using a centrifuge, clearly demonstrates that the microparticles contain predominantly poly(p-phenylene benzamide) ( $\delta$  in ppm: 168, 142, 115 - 135 assigned to carbonyl and aromatic carbons) and aminobenzoate-terminated PTHF ( $\delta$  in ppm: 71 and 27 corresponding to aliphatic ether and methylene carbons). Since polymerization consumes amine groups, whereas esterification does not affect the amine concentration, endgroup titration can be used to determine the extent of the esterification reaction at complete PAC conversion. The endgroup titration of amine and hydroxy groups reveals that at 10 wt.-% PAC content approximately 47 mol.-% of the PAC is esterified. At 8.5 wt.-% PAC content, the ester formation reaches 79 mol.-%. As a consequence, at low PAC content which is equivalent to high OH/PAC molar ratios the esterification reaction prevails, thus preventing the formation of polyaramide particles. Therefore, to obtain polyaramide dispersions, the PAC content of the PAC/PTHF mixture must exceed 10 wt.-%.

For a better evaluation of the microparticle formation, the polymerization of 20 wt.-% PAC has been carried out in triglyme at 200 °C. Since triglyme does not contain hydroxy groups, it is possible to follow the polymerization reaction by titration of the amine groups. Furthermore, the microparticles have been separated using a centrifuge. As a rough estimate of the molecular weight, the inherent viscosities of the poly(p-phenylene benzamide) have been measured in sulfuric acid. The experimental results are summarized in Table 1. After a very rapid initial conversion of the amine groups the amine conversion slows down and reaches a plateau value near 60% conversion.

Table 1. Degree of amine-group conversion and inherent viscosity of PAC-polymerization in triethyleneglycoldimethylether.

| Polymerization time<br>(min) | Amine-group conversion<br>(mole-%) | Inherent viscosity<br>(dl/g) |
|------------------------------|------------------------------------|------------------------------|
| 2                            | 25                                 | -                            |
| 4                            | 34                                 | 0.1                          |
| 7                            | 42                                 | 0.1                          |
| 13                           | 50                                 | 0.1                          |
| 22                           | 56                                 | 0.1                          |
| 30                           | 60                                 | 0.1                          |

In conclusion, the molecular weights of the poly(p-phenylene benzamide)s are quite low. In dispersion polymerization reactions, oligomers are known to phase separate in the early stage of the polymerization. Subsequently, temperatures well above 300 °C are required to increase the molecular weights in solid state polycondensation reaction (12,13). Since the quantitative separation of PTHF is not achieved, it appears quite likely that the PTHF is covalently attached to the microparticles via esterification. This may also account for the excellent stabilities of the resulting microparticle dispersions.

The polymer polyol prepared from PTHF and 10 wt.-% PAC and the corre-

sponding polymer polyols diluted with PTHF have been reacted with 4,4'-diisocyanatodiphenyl-methane at a NCO/OH molar ratio of 1.05 to produce slightly crosslinked flexible polyurethanes which do not contain additional hard segments.

Table 2. Composition and mechanical properties of polyurethane microcomposites

| Dispersed phase        | Content<br>(wt.-%) | Young's modulus<br>(MPa) | Tensile strength<br>(MPa) | Elongation to<br>break<br>(MPa) |
|------------------------|--------------------|--------------------------|---------------------------|---------------------------------|
| PAC polymer            | 0                  | 1.7                      | 6                         | 800                             |
| "                      | 1                  | 3                        | 8                         | 700                             |
| "                      | 4                  | 4.2                      | 12                        | 750                             |
| "                      | 7                  | 4.9                      | 13                        | 850                             |
| "                      | 10                 | 5.8                      | 20                        | 850                             |
| glass beads            | 17.5               | 2.3                      | 8                         | 650                             |
| PAN-particles          | 10                 | 4.5                      | 6                         | 350                             |
| PAN-particles          | 4                  | 2.3                      | 3                         | 400                             |
| PTHF-PAB <sup>1)</sup> | -                  | 6.9                      | 9                         | 500                             |

1) bis(4-aminobenzoate)-terminated PTHF

The PAC contents and the resulting mechanical properties are summarized in Table 2. For comparison, equivalent volume fractions of glass beads of 10  $\mu\text{m}$  average diameter and polyacrylonitrile/PTHF dispersion have been used. Both Young's modulus and tensile strength increase significantly with increasing PAC content. Interestingly, the elongation at break remains in the range of 800 %. In contrast, polyurethane containing 15 wt.-% glass beads (volume fraction equivalent to 10 wt.-% PAC), polyacrylonitrile-microparticles or (4-aminobenzoate)-terminated PTHF give markedly lower elongation and also lower increases of tensile strength. These results provide additional experimental evidence that the polyurethane microcomposite exhibit excellent interfacial adhesion resulting from covalent attachment of PTHF onto the microparticle surfaces. Anisotropic poly(p-phenylene benzamide)/PTHF dispersions are interesting formulation components to provide property synergisms of higher stiffness and strength without sacrificing ultimate elongation.

### Acknowledgement

The authors would like to thank Rehau AG in Rehau/Germany for financial support of this research.

**References**

- 1 Bayer O, Müller E, Petersen S, Piepenbrink HF, Windemuth E, *Angew. Chem.* 62, 57 (1950).
- 2 Meckel W, Goyert W, Wieder W in "Thermoplastic Elastomers", Legge NR, Holden G., Schroeder HE, eds., Hanser Publishers Munich 1987, 13 - 46
- 3 Dieterich D, in "Houben-Weyl Methoden der Organischen Chemie", Thieme Verlag, Stuttgart 1987, vol. 20 E, p.1583
- 4 Frisch KC, *Rubber Chem. Tech.* 53, 126 -140 (1980)
- 5 Lee LJ, *Rubber Chem. Tech.* 53, 542-599 (1980)
- 6 Vehlewald P, Volland R, *Kunststoffe* 73(8), 439-443 (1983)
- 7 Schlumpf HP, in "Plastics Additives Handbook", (Gächter R, Müller H, eds.), Carl Hanser Publ. Co., Munich 1990, 3. ed., p. 524-591
- 8 Halpin JC, *J. Composite Mater.* 3, 732 (1969)
- 9 Rösch J, Mülhaupt R, *Am. Chem. Soc., Polym. Chem. Div., Polym. Prepr.* 33(1), 370-371 (1992)
- 10 Mathias LJ, Moore DR, Smith DS, *J. Polym. Sci., Part A:Polym. Chem.* 25, 2699 (1987)
- 11 Akkapeddi MK, Housny A, Walsh MS, *Am. Chem. Soc., Polym. Chem. Div., Polym. Prepr.* 27, 120-121 (1986).
- 12 Kricheldorf HR, Ruhser F, Schwarz G, Adebahr Th, *Makromol. Chem.* 192, 2371-2381 (1991)
- 13 Kricheldorf HR, Schwarz G, Ruhser F, *Macromolecules* 24, 3485-3488 (1991)