

Synthesis of comb-like graft copolyamides with rigid aromatic main-chains and long flexible side-chains

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Summary

In this paper we report a novel method of preparing polyamide molecular composites (1) by synthesizing graft-copolymers with stiff aromatic polyamide main-chains and flexible high molecular weight (high-M) polyamides as the side chains. The unique feature of the present graft-copolyamides is that the side-chains are connected directly to the aromatic rings in the stiff polyamide chains through amide groups, and are not connected to the amide groups present in the stiff main-chains.

Introduction

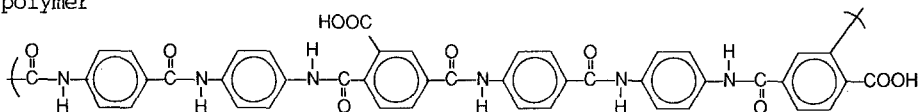
There are several reports in the literature (2–8) describing the substitution of the amide hydrogen in aromatic polyamide chains by other groups which may or may not be reacted further in a separate subsequent step. As a class, the attached groups are small. Furthermore, the replacement of hydrogen by other groups suppresses the electron delocalization in the amide groups, allows larger torsional motions around the central amide bond and, by so doing, renders the chain more flexible (9). It was therefore felt that the attachment of side-chains to the main-chain aromatic rings, instead of the main-chain amide residues, will reduce the undesirable main-chain flexibility. The syntheses of the stiff aromatic main-chains and graft-copolymers are described below. The graft copolymers and their blends with linear flexible polyamides were characterized in the bulk by means of solid-state NMR spin-diffusion techniques, x-ray diffractometry, transmission electron microscopy, DSC and rheological studies. They all indicated a single phase system in which the stiff main-chains are molecularly dispersed in the flexible side-chain matrix. Details of these investigations will be published elsewhere.

Experimental

All the stiff-chain polyamides were prepared in solution by either a single-step Yamazaki procedure (10) or a one-step Schotten-Baumann-type polycondensation. The solvent for both methods was *N,N*-dimethylacetamide (DMAc) containing 5 wt/vol % dry LiCl. The Yamazaki reactions were conducted in the 100 to 115°C temperature interval in the presence of a slight molar excess of triphenylphosphite (TPP) and pyridine. The reaction was allowed to proceed for 3 to 4 hrs. The Schotten-Baumann-type reactions were conducted in DMAc containing a small excess of pyridine for durations from 6 to 30 hours. Depending on monomer and polymer solubility, these reactions were conducted at temperatures from ambient to 85°C. After precipitation in a large

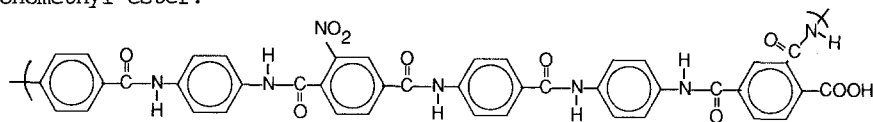
excess of methanol and purification by repeated washing in methanol, water, boiling water and acetone, the polymers were dried and readied for the next reaction.

There were altogether five kinds of stiff polyamides made, three with carboxylic acid reactive sites and two with amine reactive sites. Each kind was made in several batches having different molecular weights. The first carboxyl-containing stiff polyamide was prepared in two steps from 1:1 molar ratio of 4,4-diaminobenzanilide (DABA) and the monomethyl ester of 1,2,4-benzenetricarboxylic acid. This monoester was prepared from 1,2,4-benzenetricarboxylic acid anhydride as previously described (11). In the first step, a Yamazaki reaction was used to create the esterified polyamide which was then converted to the desired polymer



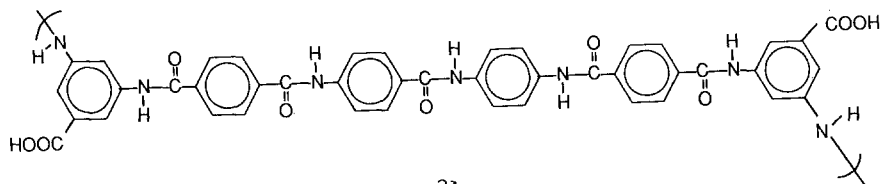
1A

by a selective hydrolysis (12) of the methyl ester groups by LiI in DMAc at temperatures higher than 150°C (11). A variant of the above, with larger average distance between the carboxy groups, was prepared in identical manner from a monomer mixture containing respectively 2:1:1 molar ratio of DABA, nitroterephthalic acid (NTPA) and the above monomethyl ester:



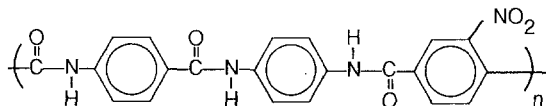
2A

The third carboxy-carrying stiff polyamide was prepared by Schotten-Baumann-type polycondensation from 1:2:1 molar ratio of DABA, terephthaloyl chloride and 3,5-diaminobenzoic acid:

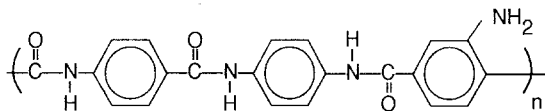


3A

The two amino-carrying stiff polyamides were prepared in two steps, the first of which was the Yamazaki procedure. The first polymer, in which every third ring is substituted, was prepared from equimolar amounts of DABA and NTPA to obtain first (13,14):

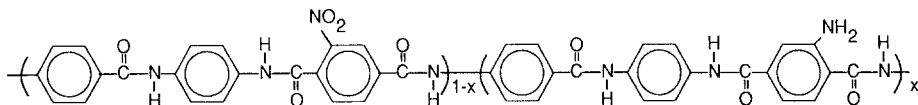


After workup and purification, this polymer was converted into the amine analogue



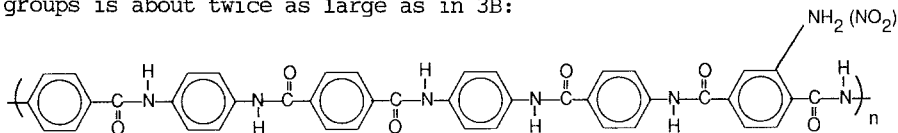
1B

by treatment with a basic solution of sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$). Accordingly, a thin stream of DMAC solution of the nitropolyamide was poured with intensive mixing into a large volume of saturated aqueous solution of sodium hydrosulfite, which was kept at a pH of about 9 by incremental additions of NaOH. The precipitated polymer was comminuted in a blender and returned to the solution. Additional increments of $\text{Na}_2\text{S}_2\text{O}_4$ were added over periods of up to 24 hrs and the pH maintained in the 8 - 9 interval. Then the whole mixture was heated to around 100°C for 2 - 3 hrs, cooled down and filtered. Infrared (IR) studies indicated that at this point the residue that was reduced to amine was complexed with the sodium hydrosulfite or a reaction by-product, and gave IR bands that could be confused with nitro bands. However, when the polymeric product was dissolved in conc. H_2SO_4 and precipitated in a large excess of ice/water mixture (careful!), then the IR spectra clearly revealed the presence of both amine and nitro groups. In general, this procedure resulted in about 1/3 or more of the nitro groups being reduced to amine. Similar results were obtained when the reduction was performed in $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}/\text{HCl}$ mixture (15). The polymers produced by both procedures look like:



2B, 3B

A similar amine-decorated stiff polyamide was obtained in identical two steps from a monomer mixture of 2:1:1 molar ratio DABA/NTPA/terephthalic acid. In this case the average distance between substituted rings is about 6 rings and the distance between amine groups is about twice as large as in 3B:



4B

For the purpose of grafting long and flexible side-chains, we used a commercial grade of polycaprolactam (nylon-6)(N6) having a weight average molecular weight of $M_w = 33,200$. The vast majority of chains in this grade of N6 are terminated by a carboxyl group on one end and an amine group on the other. Such an AB termination prevents the crosslinking and gelation of the system during grafting, making the grafting procedure described below applicable to all soluble AB-terminated flexible polyamides. It was found by us that high-M N6 nicely dissolves in DMAC/5% LiCl at elevated temperatures. Usually, a brief exposure to temperatures of ca. 135°C greatly enhances the solubility that may occur, however, even at temperatures as low as 105°C . Lower temperatures stop the dissolution of high-M N6 or make it

remarkably slow. Our preferred grafting method requires the separate dissolution of the stiff polyamide and the N6 in DMAc/5% LiCl, each at concentrations of 3 to 7 wt/vol %. The dissolution temperature of the stiff polyamide is 100 to 110°C and that of N6 is higher. The smaller volume solution was then added to the larger solution, followed by the addition of first pyridine and then TPP in slight molar excess. The reaction was then allowed to continue with constant stirring for not less than 4 hours. When the stiff polyamide carries amine groups, the reaction is best conducted at 115-120°C and when the stiff polyamide is decorated with carboxyl groups higher temperatures, up to 135°C, are preferred. (Under these conditions, a larger excess of pyridine and a reflux column should be used). After the grafting reaction was completed, the polymer was precipitated in a large excess of methanol, carefully purified and dried to constant weight.

Dilute solution viscosities were measured at 25°C on solutions of the polymers in conc. H₂SO₄ using internal dilution Cannon-Ubbelohde glass viscometers with solvent efflux times longer than 100s.

Results

To estimate the grafting efficiency of the aliphatic nylon-6 onto the aromatic stiff polyamides, the reaction products were fractionated by exhaustive room temperature extraction with 2,2,2-trifluoroethanol (TFE) which is a good solvent for N6 and a non-solvent for the stiff aromatic polyamides. Mass-balance was performed on the starting graft-copolymer, on the TFE-insoluble fraction and on the TFE-soluble fraction. It was found that in the case of carboxyl-decorated stiff polyamides the grafting efficiency of the nylon-6 was about 50% and in the case of amine-decorated stiff polyamides the N6 grafting efficiency was 85%. By grafting efficiency it is meant the fraction of all nylon-6 chains present in the reaction mixture that ended up connected to the stiff aromatic chains.

The intrinsic viscosities of representative unfractionated grafting reaction products, and the precursor linear stiff and flexible polyamides, are presented in Table I. In all depicted cases, we used a reaction mixture containing 15 wt/wt % stiff polyamide and 85 wt/wt % nylon-6. The high viscosity values of the graft-copolymers clearly indicate a substantial increase in their molecular weights relative to the respective precursor polymers proving that graft-copolymers were indeed obtained. Since the relationship between molecular weight and intrinsic viscosity is not known for the stiff-flexible comb-like graft copolymers, the absolute molecular weight of these polymers could not be ascertained. Some molecular weights of precursor polymers were determined by light scattering.

The large difference in the intrinsic viscosities of the graft copolymer 49-1 and the blend 49-6 of otherwise identical composition, clearly reflects the high grafting efficiency obtained in our procedure. Electron microscopy and solid-state NMR spin diffusion studies, to be presented elsewhere, clearly show that in the graft copolymers the stiff aromatic polyamides are not phase separated and are molecularly dispersed in the N6 matrix, while in the blend 49-6 a phase separation of the aromatic stiff chains into aggregates containing ten to twenty chains each could be detected.

Table I
 Intrinsic Viscosities and Molecular Weights of Stiff Reactive Polyamides, Nylon-6, Representative 15/85 Graft-Copolymers and a 15/85 Blend of stiff and Flexible Polyamides.

Code	Sample Description	$[\eta]$, dL/g	M_w
<u>(a) Stiff Polyamides with Carboxylic Reactive sites.</u>			
1A	Stiff Aromatic Polyamide	0.31	7,000
2A	Stiff Aromatic Polyamide	0.58	20,000
3A-1	Stiff Aromatic Polyamide	0.40	10,000
3A-2	Stiff Aromatic Polyamide	1.04	
N6	Nylon-6 flexible polyamide	1.24	33,200
20	15/85 Copolymer of 3A-2 and N6	3.30	
<u>(b) Stiff Polyamides with Amine Reactive Sites.</u>			
1B	Stiff Aromatic Polyamide	0.81	12,140
2B	Stiff Aromatic Polyamide	1.1	
3B-1	Stiff Aromatic Polyamide for series 49	0.68	
3B-2	Stiff Aromatic Polyamide for polymer 35	0.83	
4B	Stiff Aromatic Polyamide for polymer 58	0.74	
N6	Nylon-6 flexible polyamide	1.24	33,200
49-1	15/85 <u>Copolymer</u> of 3B-1 and N6	2.10	
49-6	15/85 <u>blend</u> of 3B-1 and N6. No grafts	1.10	
18	15/85 Copolymer of 2B and N6	2.35	
35	15/85 Copolymer of 3B-2 and N6	1.56	
58	15/85 Copolymer of 4B and N6	1.31	

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