

Communication: Moderate-molecular-weight copolyamides soluble in *N*-methylpyrrolidone (NMP) containing dissolved CaCl_2 can be obtained by polycondensation of terephthalic acid (TPA), *p*-phenylenediamine (PPD), and

p-aminobenzoic acid (PABA) with triphenyl phosphite/pyridine in NMP. The randomly copolymerized polymers contain more than 40 mol-% of PABA and are easily soluble in NMP.

Random copolyamides of terephthalic acid, *p*-phenylenediamine and *p*-aminobenzoic acid soluble in *N*-methylpyrrolidone/ CaCl_2

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Introduction

The terephthalic acid (TPA)/*p*-phenylenediamine (PPD) polyamide is very prominent as super high-modulus and high-strength material, but is infusible and insoluble in usual organic solvents due to the strong intermolecular hydrogen bonding between the amide bonds in the polymer chain. It is soluble only in strong acids, such as sulfuric acid, and forms a lyotropic mesophase in solution, from which it is processed into fibers and films with excellent mechanical and thermal properties. Lots of modifications by copolymerization with diamines have been reported in patents and have been reviewed.^[1] However, no copolymers exhibiting lyotropic mesophases in organic solvents have been prepared.

The polyamide of *p*-aminobenzoic acid (PABA) is known to show an anisotropic mesophase in *N,N*-dimethylacetamide that contains dissolved LiCl ,^[2] and to be capable of forming fibers with properties as excellent as those of TPA/PPD. The sequential TPA/PPD/PABA copolymer^[3] with excellent properties was prepared using 4,4'-diaminobenzanilide derived from PPD and PABA, but its solubility in organic solvents was not referred to.

As observed in thermotropic copolyamides prepared from triethyleneglycolbis(4-carboxylphenyl)ether (PPD) and PABA,^[4] the transition temperatures of these copolymers were significantly depressed by random incorporation of PABA via simultaneous charging of the monomers, but not so much when PABA was sequentially introduced using 4,4'-diaminobenzanilide. It was assumed that random distribution of PABA in the copolyamide might deviate the positions of the amide bonds and weaken the interchain hydrogen bonding. So it was expected that adequate introduction of PABA into the

TPA/PPD polymer might produce copolymers which are soluble in organic solvents and yield an anisotropic solution without disturbing their mechanical and thermal properties.

In this paper, we briefly describe the results of the direct copolycondensation of TPA, PPD, and PABA by phosphorylation reaction using triphenyl phosphite/pyridine in NMP as previously developed by us.^[5,6]

Experimental part

Materials

Terephthalic acid (TPA), *p*-phenylenediamine (PPD), *p*-aminobenzoic acid (PABA), triphenyl phosphite (TPP), LiCl , and CaCl_2 were obtained as reagent grade chemicals from a commercial source and used without further purification. *N*-Methylpyrrolidone (NMP) and pyridine were purified by vacuum distillation over CaH_2 and NaOH , respectively. The inherent viscosity was measured with 0.5% solutions in H_2SO_4 at 25 °C.

Stepwise copolycondensation of PABA (50 mol-%) with mixtures of TPA and PPD

The copolycondensation was carried out according to a procedure reported previously.^[6] To a 100 ml three-necked flask equipped with dropping funnel, nitrogen gas inlet, drying tube and magnetic stirrer, PABA (5 mmol), TPP (5 mmol), LiCl (1.0 g) and a solvent mixture consisting of pyridine (1.7 ml) and NMP (10 ml) were added. Under a nitrogen atmosphere, the mixture was heated in an oil-bath and kept at 120 °C. To the resulting solution, a solution of TPA (2.5 mmol), PPD (2.5 mmol) and TPP (5 mmol) in NMP (30 ml) that contained dissolved CaCl_2 (2.4 g) was added in one por-

tion, and the mixture was kept at 120 °C for 2 h. The resulting gel was ground in methanol to a powder, separated by filtration, washed with hot methanol, and dried.

Random copolycondensation of TPA, PPD and PABA

In a 100 ml three-necked flask equipped with dropping funnel, nitrogen gas inlet, and drying tube, PABA (6.0 mmol), TPA (5.2 mmol), PPD (5.2 mmol), TPP (10 mmol), pyridine (1.7 ml), LiCl (1.0 g) and NMP (30 ml) containing dissolved CaCl₂ (2.4 g) were placed, and the whole mixture was heated at 120 °C for 2 h under stirring and a nitrogen atmosphere. Copolymers were isolated by working up as described above.

Results and discussion

To investigate how PABA should be effectively introduced into the TPA/PPD polymer to improve the TPA/PPD/PABA copolymer, a two-stage copolycondensation of PABA (50 mol-%) followed by TPA and PPD was carried out by varying the time of oligomerizing PABA, and the solubility of the resulting copolymer in *N*-methylpyrrolidone (NMP) that contained dissolved CaCl₂ (8 wt.-%) was examined (Tab. 1). Randomly copolymerized polyamide by simultaneous charging of the three monomers revealed better solubility in the solvent system. With longer reaction time and, hence, longer PABA segments in the copolymer, the solubility of the copolymer decreased. Moreover, the solubility decreased almost completely after a period of 50 min. On subsequent reaction with TPA and PPD, the longer PABA segments would produce a copolymer with longer TPA-PPD unit segments of low solubility. This copolymer might be precipitated from the reaction mixture and left without further reaction. This is probably due to the decrease in solubility and inherent viscosity of the copolymer obtained by longer initial reaction of PABA.

Tab. 1. Stepwise copolycondensation of PABA (50 mol-%) followed by reaction with TPA and PPD.

Reaction time of PABA min	$\eta_{inh}^{a)}$	Solubility ^{b)}
0	2.51	++
20	1.86	+
30	1.79	±
40	1.59	±
50	1.54	–

^{a)} 0.5 g/dl in sulfuric acid at 30 °C.

^{b)} ++ soluble at room temperature, + soluble on warming, ± soluble on prolonged warming, – insoluble.

Tab. 2. Random copolycondensation of TPA, PPD and PABA.

PABA mol-%	PABA/TPA/PPD mol/mol/mol	State ^{a)}	$\eta_{inh}^{b)}$	Solubility ^{c)}
60	6/2/2	Solution	2.20	++
50	5/2.5/2.5	ppt (60 min)/gel (90 min)	2.51	++
40	4/3/3	ppt (50 min)/gel (90 min)	1.96	+
30	3/3.5/3.5	ppt (30 min)/gel (90 min)	2.19	±
20	2/4/4	ppt (30 min)/gel (90 min)	1.97	±
10	1/4.5/4.5	ppt (20 min)/gel (60 min)	1.89	±
0	0/5/5	ppt (20 min)/gel (60 min)	2.47	–

^{a)} ppt: precipitation.

^{b)} 0.5 g/dl in sulfuric acid at 30 °C.

^{c)} ++ soluble at room temperature, + soluble on warming, ± soluble on prolonged warming, – insoluble.

Tab. 2 shows the results of the random copolycondensation of TPA, PPD, and PABA by varying the molar percentage of PABA, as well as the solubility of the resulting copolyamides in NMP. The copolyamides having inherent viscosities of around 2.0 were obtained in quantitative yield. Most of the reactions were accompanied by precipitation of the copolymer in between 1 h followed by physical gelation. It is interesting to note that the copolycondensation involving 60 mol-% PABA proceeded homogeneously to produce a soluble polymer having a moderate inherent-viscosity value of 2.2. Incorporation of more than 50 mol-% PABA yielded copolymers which are easily soluble at room temperature, but the copolymers containing less than 50 mol-% were less soluble at room temperature, but gradually dissolved on warming.

Although the obtained copolyamides have inherent viscosities of around 2.0, these values may not be sufficient to produce fibers of commercial quality. Further study is in progress and will be reported in the near future.

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