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Synthesis and characterization of phenylquinoxaline-arylene ester block copolymers

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SUMMARY

Phenylquinoxaline-arylene ester block copolymers were prepared from phenolic hydroxyl terminated oligomers of defined molecular weight using an oligomer/monomer(s) approach, in which generation of the ester linkage coupling the blocks occurred concomitantly with the growth of the polyester block. The molecular weight of the phenylquinoxaline block was held constant at 12,900, while the stoichiometry of the arylene ester monomers were adjusted to afford copolymers containing 15, 30, and 50 wt% poly(arylene ester). These copolymers represent the first example of PPQ-based block copolymers derived from well defined phenylquinoxaline oligomers.

INTRODUCTION

Poly(phenylquinoxaline), PPQ, represents an important class of high temperature polymers (1-3). These materials show excellent thermal stability (4), high Tg (5), and good mechanical properties. In addition, PPQ is soluble in common organic solvents in a fully cyclized form, precluding the need for high temperature curing reactions. Although PPQ shows these excellent properties, it has received little attention as a component in the synthesis of block and segmented macromolecules. Indeed, a multiphase polymeric material derived from PPQ has not been reported to date. Since the synthesis and properties of block copolymers is an area of widespread interest in polymer science (6-8), we believed it would be of value to prepare and study block copolymers derived from PPQ and other polymer structures in the hope of preparing interesting new mono- and multiphase polymer systems.

There have been numerous reports concerning the synthesis of random copolymers of phenylquinoxaline with esters (6), amides (7), imides (8,9), and phenyl-as-triazenes (10). The synthesis of phenylquinoxaline based block copolymers has recieved much less attention, with PPQ-PPQ (11) and PPQ-triazene (10) as the only reported examples. The PPQ-PPQ block copolymers were prepared by preforming diamine and dicarbonyl terminated phenylquinoxaline oligomers, then mixing the two oligomer solutions, without isolation, to afford further condensation and block copolymer formation. The end group functionality of the oligomers was controlled by utilizing a stoichiometric excess of either the tetraamine or bis(dicarbonyl) monomer to obtain the diamine or dicarbonyl terminated oligomers, respectively. However, this approach does not afford well defined block copolymers, since the molecular weight of the oligomers cannot be controlled by upsetting the stoichiometry of the monomers. This is due to the pseudointerfacial nature of the polymerization (10). In addition, the oligomer end groups are limited to diamine and dicarbonyl.

The preparation of new well defined PPQ-based block copolymers required the synthesis of characterized functionally terminated phenylquinoxaline oligomers. We have recently reported the synthesis of phenolic hydroxyl terminated phenylquinoxaline oligomers suitable for block copolymer synthesis utilizing a monofunctional monomer approach (12). Although we envisage the use of phenolic hydroxyl terminated phenylquinoxaline oligomers as a source for the introduction of PPQ into a variety of block copolymer systems, our initial efforts have focused on the preparation of phenylquinoxaline-arylene ester block copolymers. In this communication we will describe the utilization of phenolic hydroxyl phenylquinoxaline oligomers in the synthesis of phenylquinoxaline-arylene ester block copolymers.

EXPERIMENTAL

General

The monomers and solvents were purified prior to use by conventional methods. A phenolic hydroxyl terminated phenylquinoxaline oligomer (I) of Mn = 12,900 was prepared in analogy to the published procedure (12). The poly(arylene ester) (II) of isophthaloyl chloride and Bisphenol-A, Bis-A, was prepared by the polycondensation of isophthaloyl chloride and Bis-A in 1,1,2,2-tetrachloroethane (TCE) with triethylamine as the acid acceptor. H NMR spectra were obtained on a Varian EM-390 utilizing deuterioterachloroethane as a solvent. IR spectra were obtained on an IBM IR/44 spectrometer.

Synthesis of Poly(phenylquinoxaline-arylene esters)(III-V)

The following procedure describes the synthesis of the 50/50 (w/w) poly(phenylquinoxaline-arylene ester) (V), and is representative of the general procedure. In a 100 ml three-neck round bottom flask, fitted with an overhead stirrer and an addition funnel, a solution of 1.29g (0.100 mmole) of **I** in 25 ml of TCE/N-methylpyrrolidinone (NMP)(99.5/0.5) was prepared by adding **I** as a powder to the TCE/NMP at 60°C. After full dissolution of **I** had occurred, the resulting clear yellow solution was cooled in an ice bath. The solution was treated with 0.7510g (3.700 mmole) of isophthaloyl chloride in 2 ml of TCE, followed by dropwise addition of 0.4 ml of triethylamine, and 12 mg of 4-(dimethylamino)pyridine (DMAP). The reaction mixture was allowed to stir for 1 h at 0°C. Bis-A (0.8220 g, 3.600 mmole) was dissolved in 1 ml of triethylamine, then diluted with 10 ml of TCE. This solution was added dropwise to the reaction solution. The solution remained a clear yellow color and became very viscous. In the case of the 85/15 (III) and the 70/30 (IV) poly(phenylquinoxaline-arylene esters), an additional 5 ml of solvent was required. The polymerization was allowed to warm to room temperature, and was vigorously stirred for 20 h. The polymer was precipitated in methanol, washed, and stirred with methanol overnight. The polymer was isolated as a yellow powder by filtration, affording 2.4 g (93 %) of **V** after drying in a vacuum oven. This procedure afforded **III** and **IV** in 90 % and 86 % yield, respectively.

Polymer Characterization

The intrinsic viscosities (single point method) of all polymer samples were determined in m-cresol utilizing a Cannon-Ubbelhodhe viscometer (25°C). The composition of the phenylquinoxaline-arylene ester copolymers was determined by H NMR by comparison of the integration for the isopropylidene methyl groups to the aromatic protons. Infrared spectra were obtained on polymer films, which were heated to 325°C to remove the solvent.

RESULTS AND DISCUSSION

The synthetic scheme used for the preparation of the phenylquinoxaline-arylene ester block copolymers was based on an oligomer/monomer(s) approach, in which the ester linkage coupling the blocks are generated concomitant with the growth of the polyester block (Scheme I). This synthetic approach has been utilized in the preparation of other block copolymer systems, e.g. sulfone-ester block copolymers (13). The polyester of isophthaloyl chloride and Bis-A was selected as the coblock since it shows good solubility in TCE, precluding possible solubility difficulties which may occur if incorporation of a fully aromatic polyester block was attempted. We planned to prepare a series of copolymers by holding the molecular weight of the phenylquinoxaline oligomer constant at 12,900, and varying the arylene ester content from 15-50 wt%.

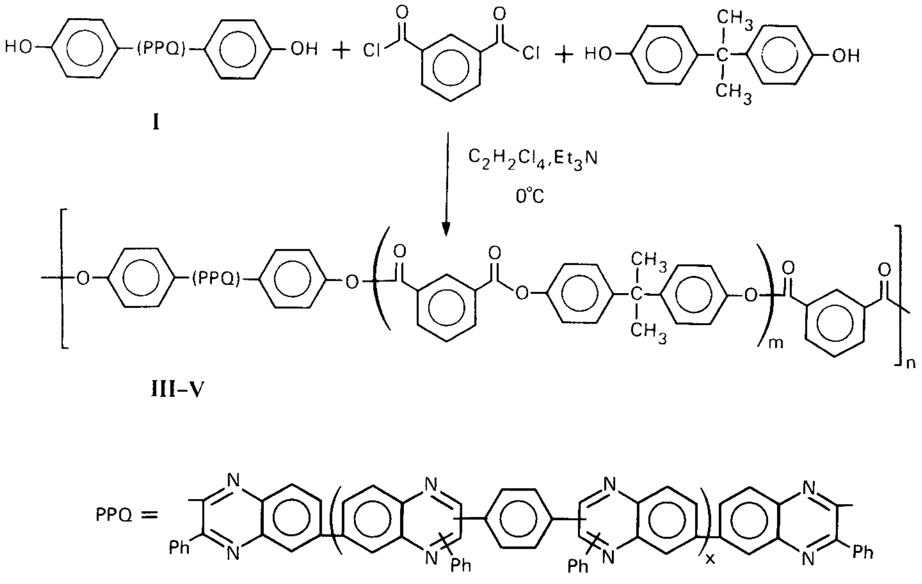
Table 1
Phenylquinoxaline – Arylene Ester Block Copolymers

Polymer	Composition (Phenylquinoxaline/Arylene Ester) Theoretical	Experimental	Yield	$[\eta]^a$
I	–	–	–	0.68
II	–	–	95	0.85
III	85/15	90/10	90	0.93
IV	70/30	75/25	86	0.84
V	50/50	55/45	93	0.82

[a] m-cresol, 25°C, concentration = 0.5g/100 cc, dl/gm.

observation that the reaction solution did not visually increase in viscosity is indicative of end capping as the major reaction course. The Bis-A solution was prepared by dissolving the Bis-A in neat triethylamine then diluting with TCE. This was necessitated by the poor solubility of bisphenol-A in TCE. This solution was added dropwise to the cold mixture of I and isophthaloyl chloride. In the synthesis of III and IV the solution became extremely viscous during the Bis-A addition, requiring further dilution with solvent to prevent polymer from climbing the stirring rod. Thus, the concentration of the polymerizations were fairly low, ranging from 5 % to 7 % solids. The polymerization mixture remained a clear, yellow color throughout the entire reaction time. The copolymers, III-V, were obtained as fibery yellow materials, becoming powders after vigorous stirring in a Waring blender.

The resulting copolymers showed good solubility in m-cresol and TCE. The solubility in TCE indicates the hydroxyl end groups have been consumed in the reaction, and no longer affect the solubility. Clear films could be cast from either m-cresol or TCE, indicating the absence of homopolymer contamination. The films were tough and fingernail creasable, consistent with good mechanical properties. The copolymer films were considerably tougher than films prepared from the phenylquinoxaline oligomer, which were not creasable. The intrinsic viscosity of the copolymers were determined in m-cresol, and were observed to increase relative to I (Table 1). The composition of the copolymers was determined by H NMR by comparison of the integration of the isopropylidene group of the polyester to the aromatic region, and showed good agreement with the theoretical values (Table 1). Bands characteristic of both PPQ and the polyester were evident in the IR spectra of III-V (Figure 1). The copolymers showed increased intensity for the polyester characteristic bands with increasing polyester content as expected (Figure 1b). The characterization data confirmed that the materials synthesized were poly(phenylquinoxaline-arylene esters) of the desired composition.



I

III-V

Scheme I. Synthesis of phenylquinoxaline-arylene ester copolymers.

The preparation of the phenolic hydroxyl terminated phenylquinoxaline oligomer (I) with a <Mn> of 12,900 was carried out by utilizing 4-hydroxybenzil as a substituted monofunctional monomer to control the molecular weight, and give the functional end groups (12). Solutions of I could be prepared in chloroform or TCE, however a small amount of NMP or triethylamine was required as a cosolvent (0.5-4%), presumably to breakup hydrogen-bonding associated with the phenolic hydroxyl end groups. A high molecular weight sample of the poly(arylene ester) (II) was prepared in TCE, confirming the suitability of this solvent for the preparation of the copolymers (Table 1).

The synthesis of the poly(phenylquinoxaline-arylene esters) was carried out by treating a solution of I in TCE/NMP (99.5/0.5) with isophthaloyl chloride and Bis-A in the appropriate stoichiometry to afford copolymers with 15, 30, and 50 wt% polyester content (III-V) (Table I). In order to ensure full incorporation of I into the resulting polymer, our approach involved the initial capping of the hydroxyl end groups of I with isophthaloyl chloride, followed by the addition of Bis-A to generate the polyester block. The capping of I was carried out by adding a solution of isophthaloyl chloride in TCE to a 5 % solution of I in TCE/NMP at 0°C. The molar excess of isophthaloyl chloride relative to I ranged between 7- and 35-fold, for III and V, respectively. Addition of triethylamine as an acid acceptor and DMAP as an acylation catalyst to the cold solution resulted in the reaction of the isophthaloyl chloride and I. Since the isophthaloyl chloride is present in excess, this will afford end capping of I as the predominant reaction rather than chain extension. The

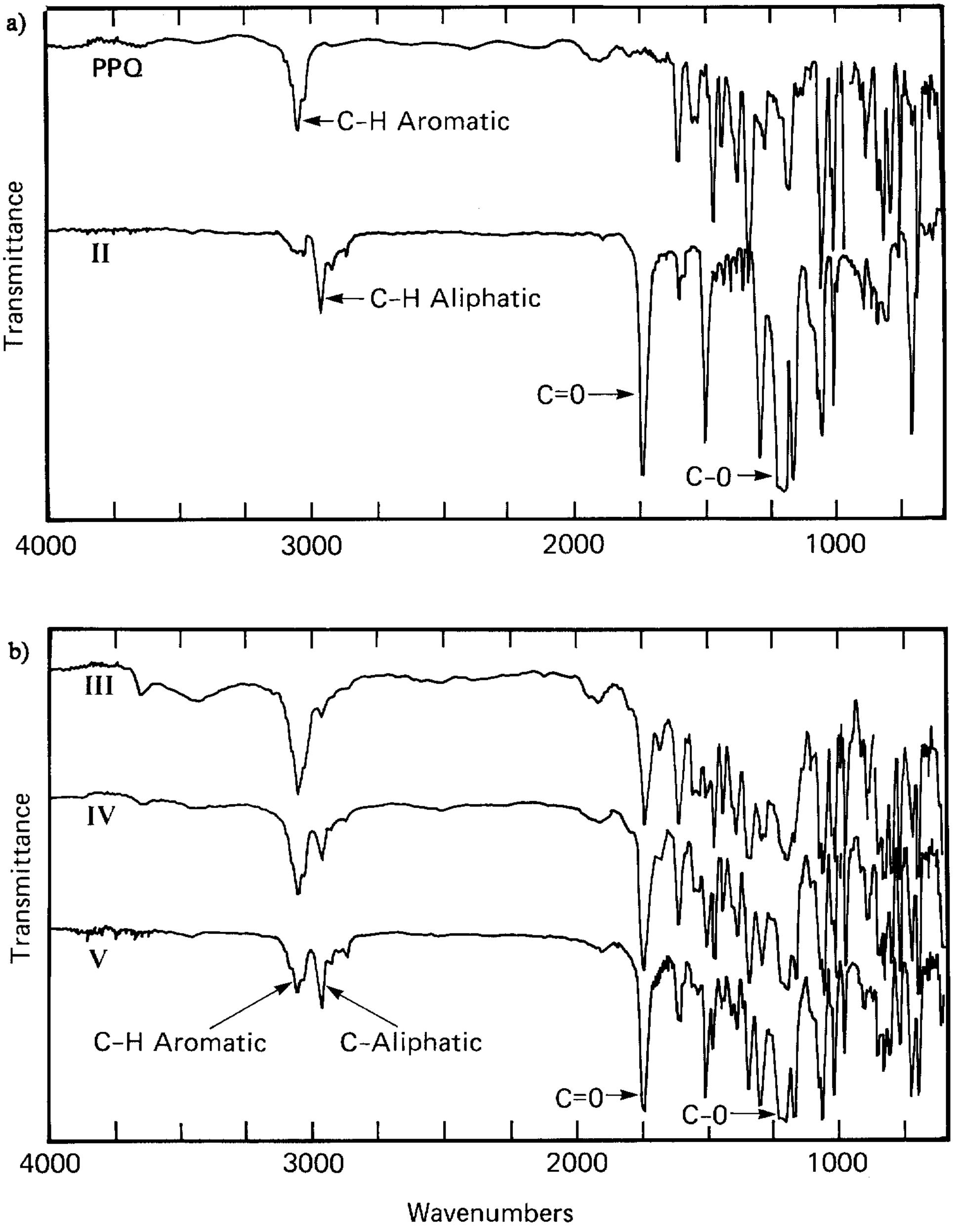


Figure 1. (a) Infrared spectra of PPQ and **II**. (b) Infrared spectra of **III-IV**.

CONCLUSIONS

The synthesis of phenylquinoxaline-arylene ester block copolymers was achieved through the polymerization of isophthaloyl chloride and bisphenol-A in the presence of a phenolic hydroxyl terminated phenylquinoxaline oligomer with a number average molecular weight of 12,900. Copolymers containing 15, 30, and 50 wt% polyarylate were synthesized. These materials represent the first example of PPQ-based block copolymers derived from well defined phenylquinoxaline oligomers. The copolymers obtained were high molecular weight, and formed clear,tough, fingernail creasable films. The affect of polyester incorporation on the polymer properties of the copolymers relative to PPQ is being investigated and will be reported elsewhere (14). Currently, we are preparing variations of the copolymers described herein by utilizing phenylquinoxaline oligomers with a range of molecular weights. In addition, we are carrying out the preparation of phenylquinoxaline-arylene ester block copolymers derived from other poly(arylene ester) structures, the results of which will be forthcoming in future publications.

REFERENCES

1. Hergenrother, P.M., Levine, H.H., J. Polymer Sci.: Part A-1, 5, 1453 (1967)
2. Wrasidlo, W., Augl, J.M., J. Polymer Sci.: Part A-1, 7, 3393 (1969)
3. Hergenrother, P.M., J. Macromol. Sci.-Revs. Macromol. Chem., C6, 1 (1971)
4. Wrasidlo, W., J. Polymer Sci.: Part A-1, 8, 1107 (1970)
5. Wrasidlo, W., J. Polymer Sci.: Part A-2, 9, 1603 (1971)
6. Hergenrother, P.M., J. Polymer Sci.: Polymer Chem. Ed., 12, 2857 (1974)
7. Duffy, J.V., Augl, J.M., J. Polymer Sci.: Part A-1, 10, 1123 (1972)
8. Augl, J.M., J. Polymer Sci.: Part A-1, 8, 3145 (1970)
9. Augl, J.M., Duffy, J.V., J. Polymer Sci.: Part A-1, 9, 1343, (197)
10. Hergenrother, P.M., J. Appl. Polymer Sci., 18, 1779 (1974)
11. Hergenrother, P.M., Appl. Polymer Symposium, 22, 57 (1973)
12. Labadie, J.W., Hedrick, J.L., Hofer, D.C., Polm. Prepr. 28(1), 69 (1987)
13. Webster, D.C., McGrath, J.E., Comtemporary Topics in Polymer Science, Vol. 4, ed. by W.J. Bailey and Teiji Tsuruta, Plenum Publishing Co., 1984
14. Hedrick, J.L., Labadie, J.W., Hofer, D.C., Polymer Bulletin, Submitted.

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