Poly(dipropargyl terephthalate): a candidate for thermosetting fibres*

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Poly(dipropargyl terephthalate), a high molecular weight linear soluble polymer, was prepared by the so-called oxidative polymerization by oxidation of the two terminal hydrogen atoms of dipropargyl terephthalate. The polymer undergoes easy thermal and radiation cross-linking via solid (crystalline) state topochemical polymerization of its two conjugated triple bonds (diacetylene linkages) of the main chain without changes in polymer crystalline lattice. This type of polymer appears attractive for preparation of (self-) cross-linkable thermosetting fibres.

(Keywords: dipropargyl terephthalate; poly(dipropargyl terephthalate); thermosetting fibres; topochemical polymerization; oxidative polymerization)

INTRODUCTION

Almost all technologically important fibres are based on linear non-cross-linkable polymers with their macromolecules oriented along the fibre axis. As a result, all fibre properties are directional. High tensile strength and modulus, observed along the fibre axis, are determined by the strength of the covalent carbon–carbon (or other) bonds of their macromolecular chains. The lower strength and modulus in the perpendicular (radial) direction are a result of the weaker intermolecular interactions (hydrogen bondings, dipolar and Van der Waal's interactions) among the fibre macromolecules. Low compressive properties, therefore, are a major short-coming of the present state-of-the-art fibres and their composites.

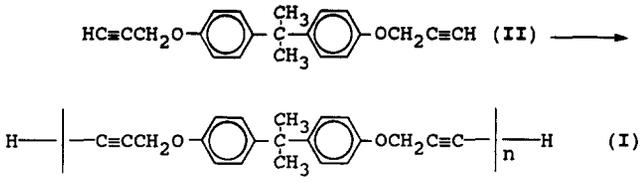
A possibility for improvement of the fibre properties in the radial direction such as compressive strength, creep resistance, etc., exists by cross-linking the fibre macromolecules. In the present paper, the preparation and initial characterization of three linear polymers with two conjugated triple bonds in the main chain are described. The research objective is the development of self-cross-linkable fibres via solid state topochemical polymerization of their diacetylene linkages.

EXPERIMENTAL

All solvents and reagents (Aldrich) were used without further purification. I.r. spectra were taken by IBM Infrared spectrometer 44.

Poly(dipropargyl bisphenol A), I

In our previous paper[1], we described the preparation and properties of poly(dipropargyl bisphenol A) (*Scheme 1*).



Scheme 1

Dipropargyl ether of bisphenol A, *II*, was prepared from propargyl chloride and bisphenol A in aqueous solution of sodium hydroxide in the presence of a small amount of tetrabutylammonium bromide as phase transfer catalyst according to the procedure described previously[2].

The polymerization of *II* was carried out employing the so-called oxidative polymerization or Glaser coupling by oxidation of the two terminal hydrogen atoms at the two triple bonds of the monomer to form two conjugated carbon–carbon triple bonds in the main chain of the polymer. The polymerization procedure is similar to that described by Hay[3,4], A mixture of dimethylformamide and pyridine was used as a solvent and copper(I) chloride as a catalyst in the presence of *N,N,N′,N′*-tetramethylethylenediamine. Oxygen gas was bubbled through the reaction mixture. The polymerization was completed in several hours at room temperature. The polymer was isolated in quantitative yield by precipitation in water. The i.r. spectra confirmed its structure and high molecular weight[1] of 15 000–25 000.

Since bisphenol A does not have a planar configuration, the obtained polymer is an amorphous polymer soluble in most organic solvents. The two conjugated triple bonds of the polymer require very low energy for radiation or thermal cure and it easily cross-links in the amorphous state. The polymer is a white powder-like material, and it stays white or very pale yellow even cross-linked by u.v.-irradiation.

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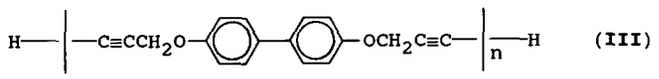


(III)

Scheme 2

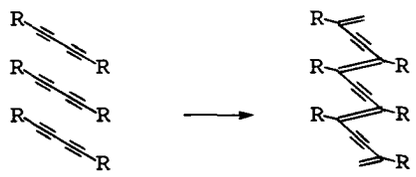
Although this polymer is soluble and undergoes easy cross-linking, it does not crystallize. Therefore, it is not suitable for topochemically cross-linkable fibres.

Poly(dipropargyl ether of 4,4'-biphenol), III

Dipropargyl ether of 4,4'-biphenol, was prepared from 4,4'-biphenol and propargyl bromide in the presence of potassium carbonate in boiling acetone according to a procedure described by Hay[3,4].

The polymer *III* (*Scheme 2*) was obtained by oxidative polymerization as described above for polymer *I*. The polymer, however, precipitated from the solution several minutes after polymerization started and we have not been able to identify solvent for it. In comparison to polymer *I*, polymer *III* has a much higher degree of symmetry and rigid rod-like structure due to the two planar benzene rings of the biphenol units and its long linear diacetylene linkages, CH_2–C≡C–C≡C–CH_2 (>6 Å). It has only two C–O bonds per monomer unit for free rotation. This presumably induces polymer crystallization from solution at an early polymerization stage (lower molecular weight).

In contrast to the white amorphous polymer *I*, polymer *III* has a darker gray (or even black) colour. This indicates that once the polymer crystallizes from solution, it undergoes a rapid solid (crystalline) state topochemical polymerization. This type of polymerization is characteristic of lower molecular weight conjugated diacetylenes:



The topochemical polymerization proceeds with the formation of long conjugated double and triple carbon–carbon bonds which cause a colour change. All known diacetylenes are reported to be polymerized topochemically without any appreciable change in the original shape and size of the crystal[5].

The premature precipitation of polymer *III* during the polymerization as a result of crystallization and cross-linking makes it no longer suitable for fibre spinning.

Poly(dipropargyl terephthalate), IV

This polymer and the monomer *V* have not been reported in the literature. Their preparation was carried out according to *Scheme 3*.

Monomer *V* (6 g) was dissolved in 40 ml dimethylformamide and added to a solution of 152 ml dimethylformamide, 48 ml pyridine, 0.12 g copper(I) chloride, and 0.2 ml *N,N,N',N'*-tetramethylethylenediamine. The solution was stirred and oxygen gas was bubbled through overnight at room temperature. The polymer was precipitated by dropwise addition to 1500 ml water, filtered and dried. Yield was 80%.

The monomer *V* was prepared by interfacial condensation. Propargyl alcohol (0.02 mol, 99%) was dissolved in 60 ml of 0.33 molar NaOH in a 500 ml beaker and vigorously stirred at 0–5°C. Terephthaloyl chloride (0.01 mol, 99+%) was dissolved in 30 ml anydrous toluene (H_2O <0.005%) and was added quickly to the propargyl alcohol solution. Stirring was continued for 2 h. The ester thus formed was filtered and washed several times with water. The small white crystals of the monomer were dried in a vacuum oven; m.p. 113°C (crude) and 117°C (recrystallized from heptane). Yields were 60–70% (white crystals).

The use of excess (10%) of propargyl alcohol does not appear to improve the monomer yield or purity, whereas the addition of phase transfer catalyst (tetrabutylammonium bromide) improves both. Monomer *V* was used for polymer preparation after recrystallization from toluene.

Several other industrially attractive procedures for preparation of monomer *V* directly from commercially available low cost dimethyl (or diethyl) terephthalate and propargyl alcohol are under evaluation.

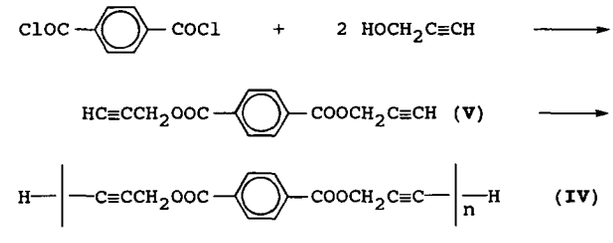
DISCUSSION

The i.r. spectra of the initial monomer *V* and its linear polymer *IV* are shown in *Figure 1*. The strong absorption band at 3253–3279 cm^{-1} (crystalline doublet) in the spectrum of the monomer corresponds to the C–H stretching vibrations of its triple bonds. This absorption band practically disappears in the spectrum of the polymer, since it does not have C≡C–H bonds. The degree of polymerization, based on the intensity of this absorption band, is more than 100, which corresponds to polymers with molecular weight in the range of 10 000–25 000.

It is well established that the C≡C stretching vibrations of mono-substituted acetylenes, C–C≡C–H are observed in the i.r. spectra as an absorption band in the range 2100–2150 cm^{-1} with medium intensity. The corresponding vibrations of the disubstituted acetylenes C–C≡C—C proceed without change in the dipole moment of their triple bonds. Therefore, they are usually not active in the i.r. spectra. In good agreement, the absorption band at 2130 cm^{-1} with medium intensity in the i.r. spectrum of the monomer, which corresponds to the C≡C stretching vibrations of its triple bonds, practically disappears in the spectrum of the polymer.

Polymer properties

In contrast to polyether *III*, polyester *IV* has more flexible macromolecules due to the free rotation around its ester groups and its shorter aromatic units. Thus, this polymer does not crystallize from the polymerization media even after storage for several days. However, it crystallizes in solid state when precipitated in water and a birefringence characteristic for crystalline polymers is observed under crossed nicols in a microscope. Once the



(V)

(IV)

Scheme 3

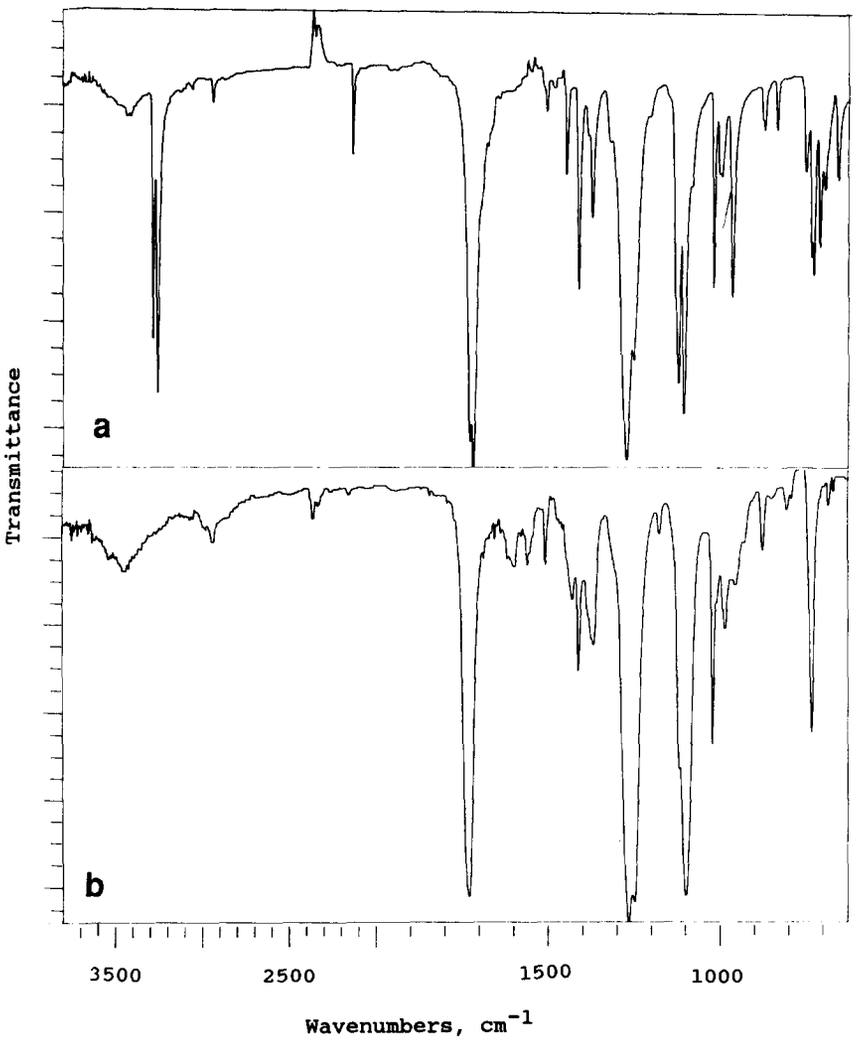


Figure 1 I.r. spectra (in KBr) of (a) dipropargyl terephthalate *V* and (b) linear poly(dipropargyl terephthalate) *IV*

polymer is crystalline, it gradually starts to cross-link and to lose its solubility. Sometimes cross-linking proceeds even during the precipitation process in water. The rate of cross-linking depends on the concentration of copper chloride used as a polymerization catalyst. Higher copper chloride concentration in the polymerization media does not appear to promote polymer cross-linking in solution; however, it leads to more rapid cross-linking of the polymer later in solid state. A small amount of copper impurity, incorporated in the polymer crystalline lattice as previously suggested for low molecular weight diacetylenes[6], probably catalyses polymer cross-linking. Lower copper chloride concentration, however, leads to incomplete polymerization and lower molecular weight polymer or longer polymerization times. Further improvement of the procedure for polymer *IV* preparation is under way in our laboratory.

Polymer *IV* thermal and u.v.-radiation cross-linking in solid (crystalline) state proceeds with a colour change from pale yellow to dark green. The polymer presumably undergoes a solid state topochemical polymerization without change in the crystalline lattice through its diacetylene units as briefly described above.

CONCLUSION

The solubility of polymer *IV*, its crystallization and cross-linking ability in solid state make it a candidate for self-cross-linkable thermosetting fibres.

Two other polymers with diacetylene linkages in their main chains, based on dipropargyl adipate and 1,7-octadiyne, are in preparation. The properties of these polymers and their application for fibre spinning is under evaluation.

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