BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 2, pp. 443–446, 1995

0032-3861/95/$10.00+0.00

Hydrophilic poly-ylids derived from 4,4′-bipyridyl: synthesis, structure and membrane-forming characteristics

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(Received 2 September 1994)

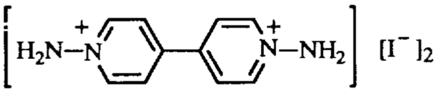
Interfacial polycondensation of 1,1′-diamino-4,4′-bipyridinium di-iodide, $[H_2N\text{–}^+NC_5H_4\text{–}C_5H_4N^+\text{–}NH_2]I_2$, with aromatic di- or tri-acyl chlorides, affords a novel class of hydrophilic polymers. These materials are isoelectronic with polyesters but contain ylid linkages $[N^-\text{–}N^-\text{–}CO]$ in place of ester bonds [C–O–CO]. Non-crosslinked polymers of this type are insoluble in conventional organic solvents but dissolve readily in proton-donor solvents such as formic and trifluoroacetic acids. Single-crystal X-ray studies of the model oligomer $C_6H_5CO\text{–}N^-\text{–}^+NC_5H_4\text{–}C_5H_4N^+\text{–}N^-\text{–}COC_6H_5$ reveal an essentially rigid-rod structure and, in keeping with this, the poly-ylids derived from terephthaloyl chloride and naphthalene-2,6-diacyl chloride exhibit lyotropic liquid crystallinity. Interfacial syntheses of poly-ylids on ultrafiltration membranes afford supported membranes with nodular morphology and useful nanofiltration properties.

(Keywords: poly-ylid; liquid crystal; X-ray)

Introduction

Polymeric membranes currently find application in a wide range of water-purification technologies including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO)[1]. Although MF and UF membranes have well characterized surface pores, with diameters of the order of 100 nm and 10 nm, respectively, the effective pore size of an NF membrane is typically around 1 nm and that of an RO membrane no more than 0.5 nm. The latter distance is beginning to approach a normal intermolecular contact, and indeed the permeation of water through an RO or NF membrane is often considered to be more closely related to diffusion through a non-porous but water-swollen polymer film than to transmission through a network of discrete pores[2]. This somewhat ambiguous nanoscale porosity seems to require that membrane polymer chains be relatively rigid, possibly crosslinked, and tenaciously hydrated, as are, for example, the aromatic polyamides used in many high-performance RO and NF membranes[3].

With these chain characteristics in mind, we have developed a new class of polymers for membrane applications based on the rigid, crosslinkable and strongly polar 4,4′-bipyridinium di-ylid linkage $[\text{–}^-N\text{–}^+NC_5H_4\text{–}C_5H_4N^+\text{–}N^-\text{–}]$. The synthetic basis of this work was established in 1967 by Downes[4], who reported the preparation of 1,1′-diamino-4,4′-bipyridinium di-iodide (**1**) and its conversion to the ylid 1,1′-bis(benzoylimino)-4,4′-bipyridine (**2**) by reaction with benzoyl chloride under Schotten–Baumann conditions. We have now extended this type of chemistry to the synthesis of polymeric ylids.



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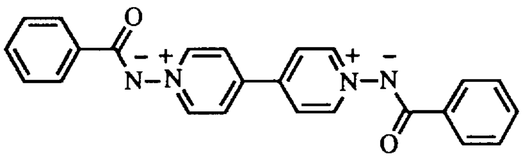

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Results and discussion

Unstirred interfacial reaction of a basic, aqueous solution of compound **1** (0.9% w/v) with isophthaloyl chloride (0.6%) in dichloromethane afforded a brilliant yellow film of polymer **3** which could be drawn continuously from the interface.

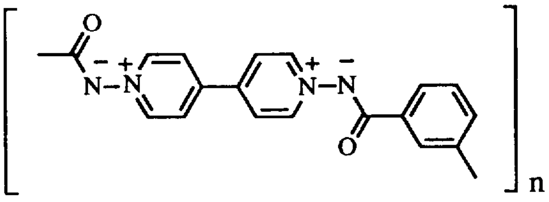

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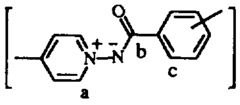
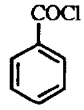
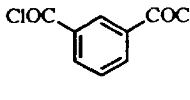
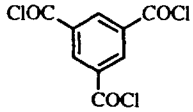
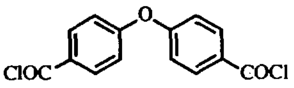
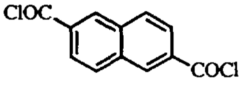
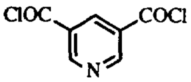
Table 1 Characterization data for the model compound **2** and for poly-ylids obtained by stirred interfacial condensation of compound **1** with aromatic acyl chlorides

Acyl chloride monomer	Polymer inherent viscosity[a]	δ ^{13}C 			I.r. (cm^{-1})	
		a[b]	*b*	*c*	ν(CO)[c]	ν(NN)
	Model compound **2**	148.1	168.4	128.7	1550	1310
	4.05	142.6	161.1	124.6	1560	1305
	Crosslinked and insoluble		–		1560	1290
	3.65		–		1550	1325
	2.62	142.4	160.9	124.1	1570	1300
	1.48		–		1570	1300
	1.99		–		1560	1300

[a] Inherent viscosity measured for a 0.1% solution in formic acid at 30°C
[b] ^{13}C n.m.r. spectra measured in *d*-trifluoroacetic acid solution
[c] Solid-state *FT*i.r. spectra measured in reflectance mode

A crosslinked poly-ylid was obtained from compound **1** by the same method, but using an equimolar mixture of isophthaloyl chloride and trimesoyl chloride, and unstirred polycondensation of **1** with pyridine-3,5-dicarbonyl chloride also gave a strong, coherent polymeric film. However, this technique was less successful with other monomers including terephthaloyl chloride, naphthalene-2,6-dicarbonyl chloride, 4,4'-oxydibenzoyl chloride, and pure trimesoyl chloride, all of which polycondensations were best carried out by stirred phase-contact in a high-shear mixer.

The resulting poly-ylids have a characteristic yellow colour and are soluble, with the exception of the crosslinked material derived from trimesoyl chloride, in strong proton-donor solvents such as formic and trifluoroacetic acids. The resulting solutions are essentially colourless, though precipitation in water regenerates bright yellow polymer, suggesting that dissolution occurs via reversible protonation at the ylid (N^-) nitrogen.

Polymers were characterized by solution viscosity measurements, ^{13}C n.m.r., and i.r. spectroscopy. Selected data are shown in *Table 1* together with data for the model compound **2**, from which it is clear that the ylid linkage does indeed predominate in the polymers reported here. Strong, broad ν(O–H) absorptions at ~3400 cm^{-1} were also evident in the i.r. spectra of these polymers, suggesting the presence of solvating water. Elemental analysis of the crosslinked polymer from trimesoyl chloride indicated an equilibrium water content of some 18 wt% at 20°C and 35% relative humidity, and gravimetric measurements of moisture regain in air showed that only about half of this solvating water could be removed by exhaustive drying at 80°C under vacuum.

The molecular structure of the model oligomer **2**, determined by single-crystal X-ray diffraction, is shown in *Figure 1**. The molecule has a crystallographic centre of symmetry, with the carbonyl groups adopting a transoid conformation and the terminal carbons C(3),

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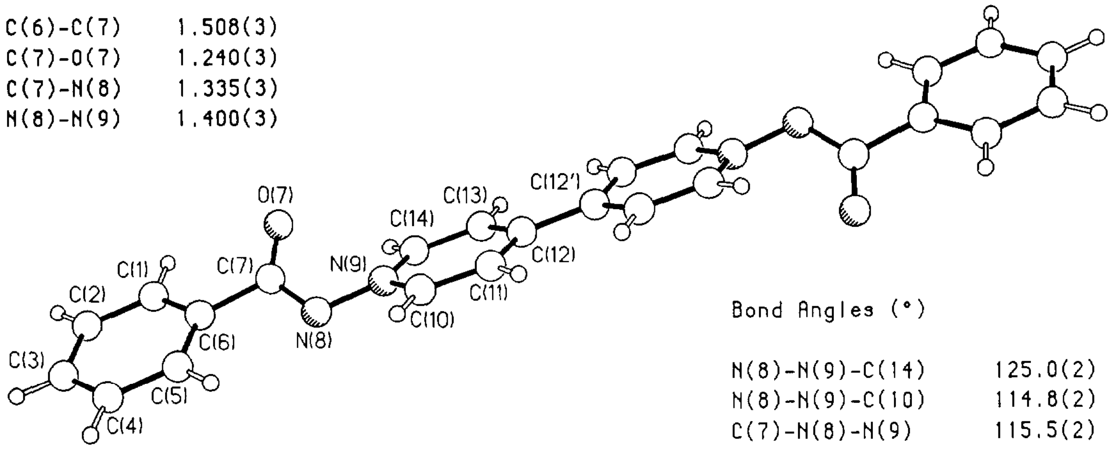
*Crystal data: $C_{24}H_{18}N_4O_2$, M = 394.4, orthorhombic, a = 10.451(3), b = 10.589(2), c = 17.377(3) Å, V = 1923.4(7) Å^3, space group *Pbca*, Z = 4 (the molecule is disposed about a centre of symmetry), D_c = 1.362 g cm^{-3}, μ(Cu-Kα) = 0.722 mm^{-1}, λ = 1.54178 Å, F(000) = 824. Data for a crystal of dimensions 0.16 × 0.16 × 0.21 mm were measured on a Siemens P4/PC diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. Of the 1296 independent reflections measured, 1013 had $|F_0| > 3\sigma(|F_0|)$ and were considered to be observed. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically to give R = 0.043, R_w = 0.043. Full details of atomic coordinates, bond lengths and angles, and thermal parameters are available from the authors on request

Bond lengths (Å)

C(6)-C(7)	1.508(3)
C(7)-O(7)	1.240(3)
C(7)-N(8)	1.335(3)
N(8)-N(9)	1.400(3)



Bond Angles (°)

N(8)-N(9)-C(14)	125.0(2)
N(8)-N(9)-C(10)	114.8(2)
C(7)-N(8)-N(9)	115.5(2)
O(7)-C(7)-N(8)	128.6(2)
C(6)-C(7)-N(8)	112.0(2)
C(6)-C(7)-O(7)	119.4(2)

Figure 1 X-ray structure of the model oligomer **2**, showing selected bond lengths and angles

C(3′) being virtually co-linear with the bipyridyl nitrogen atoms N(9), N(9′). Such co-linearity strongly suggests that poly-ylids derived from geometrically linear diacyl halides should have an essentially rigid-rod conformation and should thus have potential for mesophase formation[5]. In formic acid, concentrated (>25 wt%) solutions of the polymers obtained from terephthaloyl chloride and naphthalene-2,6-dicarbonyl chloride did indeed exhibit the intense shear-opalescence characteristic of a lyotropic liquid-crystalline phase[6]. This phenomenon was not observed for poly-ylids derived from non-linear monomers such as isophthaloyl chloride.

Supported ('composite') poly-ylid membranes were fabricated by interfacial condensation at the surface of an ultrafiltration membrane. The support used was a commercially available polyethersulfone (PES) UF membrane from Bioken Inc., with a nominal molecular weight cut-off (*MWCO*)* of 10000 daltons. This was soaked in a 1% (w/v) solution of compound **1** in 0.08 M aqueous sodium hydroxide, drained, and the membrane surface then contacted for 20 s with a 0.1% (w/v) solution of trimesoyl chloride in hexane. The resulting bright yellow composite membrane was rinsed in deionized water and characterized in terms of its permeability to water, *MWCO*, rejection properties for sodium chloride, and surface morphology.

In crossflow reverse osmosis at 40 bar, this membrane (A) gave a water flux of 375 $\mathrm{l\,m^{-2}\,h^{-1}}$ and a rejection for sodium chloride (2000 ppm) of 50%. The *MWCO* of the membrane at 5 bar was 380, determined by measuring rejections of glucose (*MW*=180), sucrose (*MW*=342), raffinose (*MW*=504) and stachyose (*MW*=666) in a mixed feed (1000 ppm of each saccharide). The characteristics of poly-ylid composite membranes are markedly dependent on the nature of the supporting UF membrane. For example, a membrane (B), fabricated as for A, but on a UF support which had been machine-cast from Udel polysulfone* rather than from PES, showed very much higher salt rejection (83%), somewhat lower permeability to water (185 $\mathrm{l\,m^{-2}\,h^{-1}}$ at 40 bar), and a significant reduction in *MWCO* to around 300 daltons. Nevertheless, the ranges of water flux, *MWCO*, and salt rejection place both types of membrane firmly in the nanofiltration class, i.e. with an effective pore-size of approximately 1 nm (ref. 7).

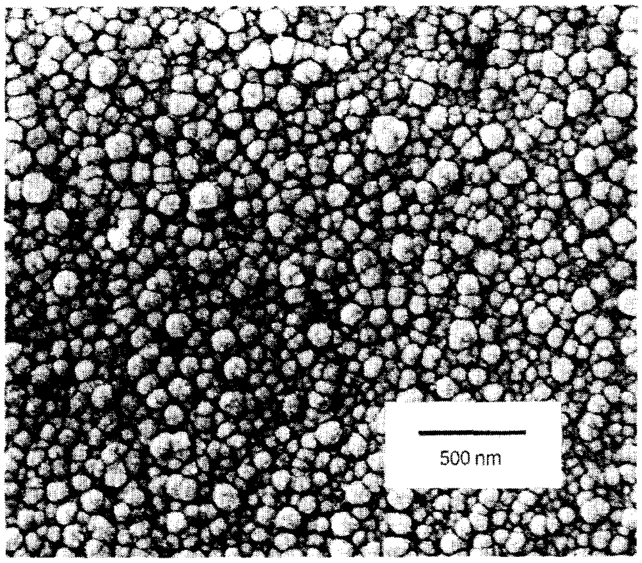


Figure 2 Scanning electron micrograph showing the nodular surface morphology of a composite nanofiltration membrane formed by interfacial polycondensation of compound **1** with trimesoyl chloride

Examination of the surface of membrane A using high-resolution scanning electron microscopy (*Figure 2*) showed a unique nodular morphology with an average nodule diameter of some 100 nm. In contrast, polyamide membranes obtained by interfacial polycondensation of aliphatic amines with trimesoyl chloride are reported to

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* *MWCO* is here defined as the lowest molecular weight of a solute for which the membrane shows >90% rejection

* Udel is a trademark of the Amoco Corporation

be relatively smooth and featureless at this scale, and analogous membranes produced from aromatic amines have convoluted surfaces with numerous microvilli-like protuberances[8]. A freeze-fractured specimen of the poly-ylid membrane revealed an average cross-section for the interfacially polymerized layer of ~50 nm. The thickness of this layer could be increased considerably by increasing the time for which the reactants were in contact, but this served mainly to reduce the water flux of the membrane without producing substantial changes in *MWCO* or salt rejection.

Conclusions

Interfacial polycondensations of 1,1′-diamino-4,4′-bipyridinium di-iodide with aromatic di- or tri-acyl chlorides afford hydrophilic polymers, isoelectronic with polyesters but based on the polar ylid linkage [N^+–N^-–CO] in place of the ester bond [C–O–CO]. Poly-ylids derived from geometrically linear diacyl halides, such as terephthaloyl chloride, exhibit lyotropic liquid crystallinity. Interfacial syntheses of poly-ylids on ultrafiltration membranes afford supported membranes with nodular morphology and good nanofiltration properties.

Acknowledgements

We wish to thank Miss E. E. Reinhardt and Mr D. F. Lewis for experimental assistance, Mr A. F. Simpson for molecular weight cut-off measurements, and Dr G. T. Finlan for scanning electron microscopy.

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