Synthesis and characterization of polymer supports carrying isocyano groups

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The synthesis of a series of beaded polymer supports carrying isocyanide groups (isocyano polymers) is described. The new polymer supports are based on polystyrene (1), polydimethylacrylamide (2), copoly(styrene–acrylate)s (3), copoly(styrene–acrylamide)s (4) or copoly(dimethylacrylamide–acrylate)s (5). All of the isocyano-carrying polymers were produced from the corresponding formamido resins by treatment with 4-toluenesulphonyl chloride. The formamido resin precursors for 1–4 were obtained by derivatization of commercially available or previously described polymers. Formamido precursors of type 5 isocyano resins were produced by direct incorporation of formamidoalkyl acrylates by suspension copolymerization. Polymer characterization and the contrasting swelling behaviour of different polymer types in water and common organic solvents were also briefly discussed.

(Keywords: macromolecular isocyanides; beaded polymer supports; copoly(styrene–trichlorophenyl acrylate); reactive acrylates; polymer derivatization; reactive polymers; polymer swelling)

INTRODUCTION

Owing to its formally divalent carbon atom, the isocyano (isonitrile) functionality exhibits a unique pattern of chemical reactivity. Among the various reactions[1] of the isocyano group, the four-component condensation (4CC) reaction and coordination with transition metals are of particular interest. The 4CC of isocyanides with an amine, a carboxylic acid and an aldehyde leads to the formation of an amide bond, and hence opens up a novel synthetic route to peptides[2] and antibiotics[3]. The isocyano group forms a wide range of coordination compounds (complexes)[4] with low-, medium- and high-valence transition metals, and is therefore of potential interest in homogeneous catalysis[5].

In the past 20 years the use of insoluble polymeric materials (polymer supports) has had a significant impact on the synthesis and sequencing of biological macromolecules[6,7] and the utilization of biocatalysts[8]. Hopes of similar developments[9,10] in homogeneous catalysis by polymer-supported transition-metal complexes have not yet been fulfilled, nor have they been abandoned.

In 1980 we initiated[11] an investigation on the development of tailor-made isocyano polymer supports for solid-phase peptide synthesis by 4CC. Our preliminary results on the preparation of isocyano polymers[12] and peptide formation[13] on isocyano polymer supports have been previously published. Since then, isocyano polymers have been found to be particularly suitable for the preparation of polymer-supported transition-metal complexes[14–16]. Isocyano derivatives of conventionally available polymer supports have also been reported by several groups[17–19]. In this paper we describe full details of our work on the synthesis of a wide range of tailor-made isocyano-carrying polymers based on polystyrene (1), poly(dimethylacrylamide) (2), copoly(styrene–acrylate)s

(3), copoly(styrene–acrylamide)s (4) or copoly(dimethylacrylamide–acrylate)s (5).

Note that the terms 'macromolecular isocyanides' or 'isocyano polymers' have been adopted for polymers *carrying* isocyano groups as described in this paper. The polymers obtained by polymerization of isocyanides:

$$nRN{\equiv}C \rightarrow -\!\!\begin{matrix} (C-)_n \\ \| \\ NR \end{matrix}\!\!-$$
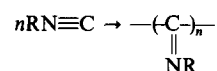
are appropriately named 'polyisocyanides', and the two classes of polymers should not be confused. For recent literature on polyisocyanides see ref. 20.

RESULTS AND DISCUSSION

The chemical formulae of the isocyano polymer to be discussed here are shown in *Scheme 1*. The polymers were derived from beaded resins based on polystyrene (1), poly(dimethylacrylamide) (2), or the copolymer structures 3–5.

Styrene-based resins (1) were either commercially available or were synthesized in the laboratory as described previously[21]. The development of dimethylacrylamide-based resins (2) has been fully discussed recently[22], and some of these resins are also commercially available[23]. The copolymer resins 3 and 4 were derived from a general-purpose activated resin[24], copoly(styrene–2,4,5-trichlorophenyl acrylate). Copolymer resins of type 5 were specially designed for the preparation of isocyano polymer supports, as will be discussed below.

Generation of the isocyano functionality on all of the polymers 1–5 was accomplished in a final step by dehydration of the corresponding formamido polymers. Among the various dehydrating agents[25,26] for the preparation of low molecular weight isocyanides, diphosgene[27] and toluenesulphonyl chloride (TosCl)[28] were examined and both were found to be effective.

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Scheme 1

1

2 (n = 1,2 or 6)

3 : X = O   **4 : X = NH**

5 (n = 1,2 or 6)
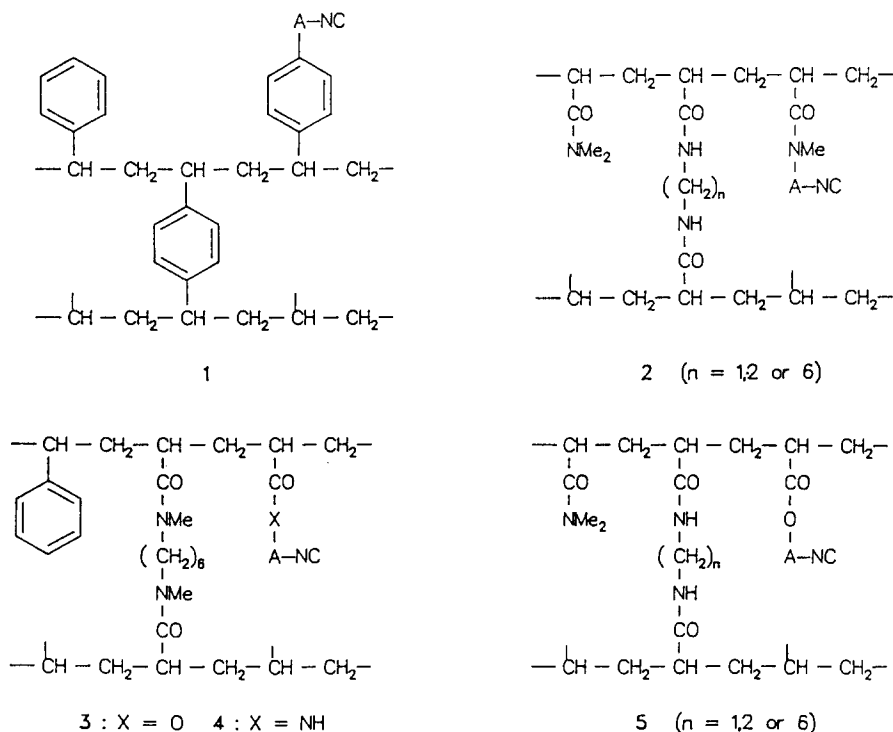
However, the use of TosCl in pyridine was found to be more convenient and was employed throughout the work. A concentrated solution of TosCl in pyridine with a large excess of the reagent was generally used, and the reaction was carried out at 0–20°C. Under these conditions, all of the described resins swelled adequately in the reagent, and the reaction was usually complete within 2–5 min for resin types **1** and **3–4**, and within 1–2 min for resin types **2** and **5**.

Styrene-based polymers (**1**)

The styrene-based isocyano polymers **1a** and **1b** (see *Table 1*) were obtained from the corresponding hydroxy-methyl polymers[21], as indicated in *Scheme 2*. The

Scheme 2

$$
\boxed{P}\!-\!\!\!\bigcirc\!\!\!-\!CH_2OH \xrightarrow[\text{2. Dehydration}]{\text{1. } (HCONHRCO)_2O} 1
$$
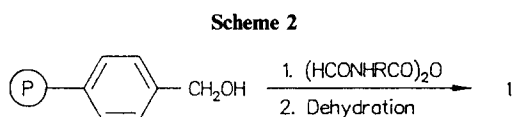
acylation reactions were carried out by using the *in situ* formed *N*-formylamino acid anhydrides in the presence of 4-dimethylaminopyridine as a catalyst[29]. The isocyano resin **1c** was prepared by using the *N*-hydroxysuccinimide activated ester of *N*-formylglycine (For-Gly-OSu) in the presence of triethylamine as a catalyst. In either case, the polymers were reacted with excess acetic anhydride to block any unreacted hydroxyl groups before dehydration with TosCl.

Dimethylacrylamide-based resins (**2**)

These polymers were prepared by formylation of the corresponding amino resin precursors[22], and subsequent dehydration of the resulting formamides. The formylation reaction was effected by refluxing the resins with methyl formate in methanol, in the presence of triethylamine. Complete formylation was ascertained by the ninhydrin test[30].

Copoly(styrene–acrylate)s (**3**)

The isocyano polymers **3a** and **3b** were derived from a beaded 1:1 copolymer[24] of styrene and 2,4,5-trichloro-phenyl acrylate according to *Scheme 3*. *Trans*-esterification
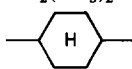
Scheme 3
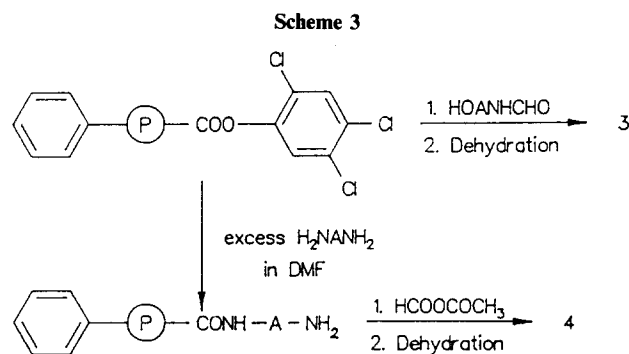
of the activated resin was carried out by using an 8–10 fold excess of the formamido alcohol in dimethylform-amide, in the presence of triethylamine at 95°C for 24 h. I.r. spectroscopy and chlorine analysis showed that under these conditions about 90% of the trichlorophenoxyl groups are displaced by the formamido alcohols. These results were confirmed by the isocyano contents of the polymers (see *Table 1*). The residual trichlorophenoxyl groups were readily displaced by treatment of the reaction mixture with excess diethylamine. Complete *trans*-esterification was accomplished by repeating the reaction, rather than by prolonging the reaction time (see ref. 24).

Copoly(styrene–acrylamide)s (**4**)

These polymers were also prepared from the activated resin according to *Scheme 3*. Formylation of the free amino groups on the polymers shown in *Scheme 3* was effected more efficiently by using formic acetic anhydride (formed *in situ*) instead of methyl formate.

Aminolysis of the activated resin with the non-symmetric diamine, *p*-aminophenethylamine, was carried

Table 1 Details of representative examples of isocyano-carrying polymers 1–5

Polymer	Spacer arm (A) in structures 1-5	Nitrogen content (%)[a]	Isocyano content (mmol g^{-1})[b]			Characteristic i.r. bands[e] (other than v_{NC} at 2150 cm^{-1})
			Calculated[c]	Br$_2$ method	HSCN method	
1a	CH$_2$OOCCH$_2$	1.65	0.93	–	0.96	1607 m, 1725 s
1b	CH$_2$OOC(CH$_2$)$_5$	–	0.70	–	0.72	1607 m, 1725 s
1c	OOCCH$_2$	1.66	0.89	–	0.88	1607 m, 1767 s
2a	CH$_2$CONHCH$_2$CH$_2$	–	0.62	0.60	–	1630–1690 b
2b	CH$_2$CH$_2$CH$_2$	–	0.66	0.58	–	1630–1690 b
3a	CH$_2$CH$_2$CH$_2$		–[d]	2.85	–	1607 w, 1640 b, 1725 s
3b	(CH$_2$)$_6$	–	3.03	2.96	–	1607 w, 1722–1730 s
4a	CH$_2$CH$_2$	8.10	–[d]	1.32	–	1607 w, 1670–1700 b
4b	(CH$_2$)$_6$	7.35	–[d]	1.51	–	1607 w, 1670–1690 b
4c	CH$_2$CH$_2$—⟨benzene⟩—	9.40	3.30	–[b]	–[b]	
5a	CH$_2$CH$_2$CH$_2$	–	2.61	2.60	2.84	1630–1690 b, 1720–1730 sh
5b	CH$_2$CH$_2$CH$_2$	–	0.59	0.50	0.63	1630–1690 b, 1720–1730 w,sh
5c	CH$_2$(CH$_3$)$_2$	–	0.74	0.50	0.57	1630–1690 b, 1720–1730 w, sh
5d	—⟨H⟩—	–	2.35	1.80	2.11	

[a] The polymers analysed for N$_2$ contain ~0.1–0.2% nitrogen derived from the initiator (AIBN) used for polymerization
[b] The isocyano content of the polymers gradually decreases under normal laboratory conditions with a half-life of about one year, but relatively rapidly in the case of 4c
[c] Based on the functionality of the starting polymer
[d] No exact calculation can be made, but the observed values were in good agreement with chlorine analysis
[e] m, medium; s, strong; w, weak; b, broad; sh, shoulder

out under relatively mild conditions at 20–35°C. Under these conditions, the activated resin does not[24] react with aromatic diamines, and the aminolysis proceeds exclusively at the aliphatic amino group. The nitrogen and isocyano contents of the final polymer (see *Table 1*) are in good agreement with the expected reaction pattern.

In the case of the symmetric diamines, 1,2-diamino-ethane and 1,6-diaminohexane, the aminolysis leads to extensive intra-resin crosslinking. As a result, the isocyano resins 4a and 4b have a more highly crosslinked and rigid structure than 4c (or 3a and 3b). Both nitrogen analysis and the isocyano contents of the polymers (see *Table 1*) show that more than 50% of the diamines that react with the activated polymer are involved in crosslinking.

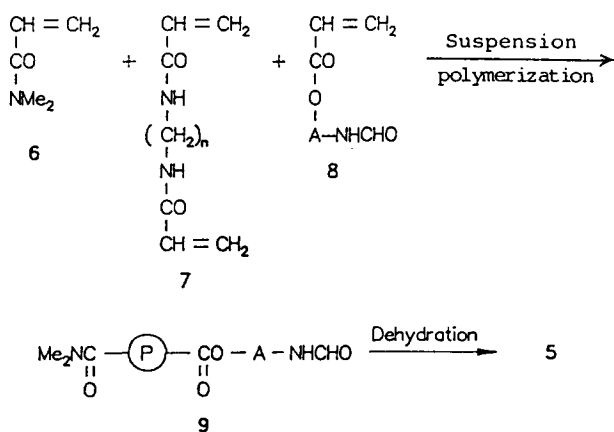### Copoly(dimethylacrylamide–acrylate)s (5)

The formamido precursors of type 5 isocyano resins were prepared by suspension copolymerization of di-methylacrylamide (6), a bisacrylamide crosslinker (7) and the formamidoalkyl acrylate monomer (8) (see *Table 2*), according to *Scheme 4*. Suspension polymerization was

carried out at 50°C by essentially the same procedure as described for dimethylacrylamide-based polymers[22]. In this procedure, a mixture of water and dimethylformamide was used as a monomer diluent (polymerization solvent), ammonium peroxydisulphate as initiator, 1,2-dichloro-ethane as suspension medium and cellulose acetate butyrate as a suspension agent. Under these conditions, the polymers were obtained in the form of small beads (~100–200 μm) with yields of 80–95%.
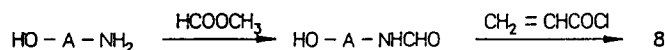
Quantitative details for the preparation of a number of formamido resins (9) by suspension copolymerization according to *Scheme 2* are given in *Table 3*. The exact compositions of the formamido resins (9) cannot be readily deduced from microanalysis. However, the iso-cyano contents of the resins (see *Table 1*) indicate that, under the adopted experimental conditions, polymer composition is practically the same as that of the initial monomer mixture.

The formamidoalkyl acrylates (8) used for the prepar-ation of the formamido resins (9) were synthesized from the corresponding amino alcohols, as indicated in *Scheme 5*. Selective formylation of the amino function in
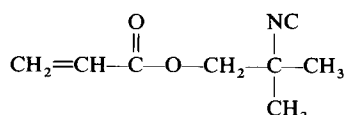
Scheme 4

7

Me$_2$NC —⟨P⟩— CO – A – NHCHO $\xrightarrow{\text{Dehydration}}$ 5

9

Scheme 5

HO – A – NH$_2$ $\xrightarrow{\text{HCOOCH}_3}$ HO – A – NHCHO $\xrightarrow{\text{CH}_2 = \text{CHCOCl}}$ 8

the presence of the hydroxyl group was accomplished by using methyl (or ethyl) formate in methanol, in the presence of triethylamine, at room temperature. The boiling (or melting) points of a series of formamidoalkyl acrylates and their corresponding formamido alcohols are given in *Table 2*. Among these, 4-formamidocyclo-hexanol, 4-formamidocyclohexyl acrylate (8e) and the amino alcohol precursor used for their synthesis showed a relatively wide distillation range, presumably representing a mixture of isomers.

The formamidoalkyl acrylates (8) can be converted to

the corresponding isocyano derivatives via dehydration of the formamido function. Dehydration of **8b** to 2-isocyano-2-methylpropyl acrylate (**10**) by diphosgene is described in the 'Experimental' section, and that of **8a** by $POCl_3$ is reported recently by Corain *et al.*[25]. Copolymerization of **10** with **6** and **7** in aqueous solvents produced the corresponding formamido resin, rather than the expected isocyano resin. However, (co)polymers of **10** were produced readily under non-aqueous conditions. Aqueous polymerization of isocyanoalkyl acrylates can probably be carried out at low temperatures to avoid thermal hydration of the isocyano function.

$$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}\overset{\overset{NC}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}CH_3$$

10

Polymer characterization

The main polymer characteristics, namely the isocyano

contents of the resins, were determined by bromination and/or thiocyanation, as described previously[31,32]. The results are given in *Table 1*.

Infra-red (i.r.) spectroscopy of the polymers provided a valuable analytical tool for the monitoring of the various polymer derivatizations discussed above. It was also found useful for qualitative estimates of the isocyano groups on the polymers. The isocyano group generally exhibits a narrow stretching vibration at about $2150\,cm^{-1}$, well separated from other absorptions in the spectrum. Characteristic absorptions other than v_{CN} for different polymers, namely polystyrene backbone $(1607\,cm^{-1})$, ester carbonyl $(1720{-}1730\,cm^{-1})$ and amide carbonyl $(1630{-}1690\,cm^{-1})$, are given in *Table 1*. These could usually be used as internal standards, hence facilitating routine analysis of the isocyano groups on the polymers.

Polymer swellability

The swelling behaviour of representative examples of the isocyano polymers **1–5** is given in *Table 4*. Polymer swellability was measured by equilibrating the samples with the indicated solvents, and reading the bulk expanded volume (bed volume). The swellability data in *Table 4* are intended primarily to illustrate the pattern of solvent compatibility of the polymers, rather than the extent of polymer swelling. For each polymer type, less or more highly swellable samples can be produced readily by adjusting the composition of the monomer mixture and/or the polymerization conditions (see refs. 21, 22 and 24).

The contrasting swelling behaviour of different resin types is obviously related to the chemical structure of the polymers (see *Scheme 1*). However, the swellability data cannot always be explained on the basis of polymer/solvent polarity. For example, the polar solvent tetrahydrofuran (THF) is compatible with the non-polar resin

Table 2 Characteristics of formamidoalkyl acrylates

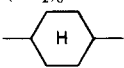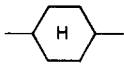(**8**, $CH_2{=}CHCOO{-}A{-}NHCHO$)

and their formamido alcohol precursors

Monomer (8)	A	Boiling point	
		Monomer	Formamido alcohol
8a	$CH_2CH_2CH_2$	142°C/2 mmHg	151°C/2 mmHg
8b	$CH_2C(CH_3)_2$	115°C/0.6 mmHg m.p. 31°C	m.p. 70–72°C
8c	$CHCH_2$ | CH_2CH_3	Not determined	142°C/0.5 mmHg
8d	$(CH_2)_6$	Not determined	m.p. 45–46°C
8e	—⟨H⟩—	~154°C/0.3 mmHg	~170°C/0.3 mmHg

Table 3 Typical compositions used for the preparation of formamido resins (9) by water-in-oil suspension copolymerization of the monomers 6–8

Formamido polymer (9)	Monomer 7		Monomer 8		$H_2O{-}DMF^a$	
	n	mol%	A	mol%	$H_2O{:}DMF$ ratio	ml/g monomer
9a	2	5.4	$CH_2CH_2CH_2$	35.1	1:1	3.0
9b	6	7.8	$CH_2CH_2CH_2$	33.6	1:1	3.1
9c	6	7.8	$CH_2CH_2CH_2$	33.6	2:1	3.0
9d	2	7.7	$CH_2CH_2CH_2$	6.3	2:1	3.0
9e	1	8.0	$CH_2C(CH_3)_2$	8.0	2:1	3.0
9f	1	6.0	$CH_2C(CH_3)_2$	29.3	1:1	3.4
9g[b]	6	7.7	—⟨H⟩—	33.0	2:1	3.1

[a] Water–dimethylformamide (DMF) was used as a monomer diluent

[b] Prepared by solution (i.e. homogeneous) polymerization, followed by grinding of the bulk polymer to produce small particles

Table 4 Swelling behaviour of representative examples of isocyano polymers 1–5 in different solvents

Polymer type	Bulk expanded volume $(ml\,g^{-1})^a$ in different solvents[b]						Ref.
	EtAc	THF	DCM	DMF	MeOH	H_2O	
1	4.8	5.0	5.5	4.4	no	no	21
2	no	no	9.5	9.1	12	9.0	22
3	9.0	9.8	11	9.1	sl	sl	24
4	sl	sl	4.3	4.7	4.0	2.0	24
5	sl	sl	10	10	9.5	10	This work

[a] no and sl indicate no or slight polymer swelling, respectively

[b] EtAc, ethyl acetate; THF, tetrahydrofuran; DCM, dichloromethane; DMF, dimethylformamide; MeOH, methanol

(1), but not with the polar resin (2). More comprehensive swellability data for polymers of type 2^{22} and 3, 4^{24} and a fuller discussion on the polymer structure–swellability relationship have been presented elsewhere.

EXPERIMENTAL

Materials

Acetic anhydride, formic acid, methyl formate, dichloromethane (DCM), dimethylformamide (DMF) and 4-toluenesulphonyl chloride (TosCl) were reagent or analar grade obtained from EGA Chemie or Fluka. Polystyrene[21], poly(dimethylacrylamide)[22] and copoly-(styrene–2,4,5-trichlorophenyl acrylate)[24] samples were prepared as described previously. *N*-Formylglycine was provided by Dr H. von Zychlinsky. All other chemicals and solvents were general-purpose reagents and were used as received from the suppliers.

Analysis

Infra-red spectroscopy of the crosslinked polymers was carried out as described previously[24]. Chlorine and sulphur analyses were performed by Bernhardt (Bonn, FRG). Isocyano titration was carried out as described previously[32].

Polymer swelling

The polymer sample (0.5–1.0 g) was equilibrated with excess solvent in a graduated tube cell fitted with a sinter base and a suction tap. The polymer was well mixed with solvent by means of a spatula and the mixture was allowed to stand at room temperature for 15 min. The bulk expanded volume of the polymer sample was then read directly from the graduated tube.

6-(N-*Formylamino*)hexanoic acid

Formic acid (20 ml) was added dropwise (5 ml min^{-1}) to an equal volume of acetic anhydride with gentle stirring. The mixture, which became hot, was allowed to cool to room temperature, and 6-aminohexanoic acid (13.19 g, 100 mmol) was added in small portions. A clear solution was obtained after about 10 min. This was allowed to stand at room temperature for 24 h. The product that crystallized during this period was separated by decantation. The remaining solution was kept at 0°C for 6 h, followed by decantation and separation of the crystalline product. The two crystalline fractions were combined, washed with dry diethyl ether (× 5), and dried in a vacuum oven at 35°C. The yield was 11.59, 72%, m.p. 115–116°C.

Analysis for $C_7H_{13}NO_3$: calc.(%), C 52.88, H 8.18, N 8.80; found(%), C 52.42, H 8.23, N 8.54.

3-Formamidopropyl acrylate (8a)

A solution of 3-aminopropanol (37 g, 0.5 mol) in methanol (200 ml) and triethylamine (10 ml) was stirred in a 500 ml round-bottomed flask with a condenser and a dropping funnel. Methyl (or ethyl) formate (1.8 mol) was added dropwise over 30 min (exothermic reaction). The reaction mixture was then allowed to stand at room temperature overnight (15 h). Most of the solvent and excess reagent were removed under reduced pressure at 40°C. The residue was distilled under reduced pressure (b.p. 151°C/2.5 mmHg), or subjected to co-evaporation with chloroform (3 × 40 ml) on a Rotavapor at room temperature. The distilled (or crude) 3-formamidopropanol thus obtained was dissolved in DCM (180 ml). Triethylamine (56 g, 0.55 mol) and 4-dimethylaminopyridine (0.8 g) were added, and the solution was stirred in an ice bath. Acryloyl chloride (47.5 g, 42.8 ml, 0.52 mol) in DCM (50 ml) was added over 45 min, and the mixture was allowed to stir overnight at ambient temperature. The reaction mixture was then washed with $NaHCO_3$ solution (9%, 4 × 15 ml), hydrochloric acid (1 M, 20 ml) and saturated sodium chloride solution (4 × 15 ml). The solution was dried over magnesium sulphate, filtered and the solvent removed under reduced pressure. The residue (68 g) was distilled in the presence of picric acid (0.45 g) to produce the product, 3-formaminodopropyl acrylate (8a, b.p. 122°C/0.23 mmHg or 141°C/2 mmHg). The yield was 41.6–53% based on the amino alcohol.

Analysis for $C_7H_{11}NO_3$: calc.(%), C 53.50, H 7.01, N 8.92; found(%), C 53.33, H 7.04, N 8.53.

Other formamidoalkyl acrylates listed in *Table 2* were prepared by the same procedure as described above.

2-Isocyano-2-methylpropyl acrylate (10)

2-Formamido-2-methylpropyl acrylate (2.5 g, 15 mmol) in DCM (50 ml) and triethylamine (3.5 g, 35 mmol) was stirred in a water bath (15°C). Diphosgene[27] (1.59 g, 7.5 mmol) in DCM (30 ml) was added dropwise over 30 min, and the reaction mixture was kept at ambient temperature for 2.5 h. The reaction mixture was then washed with 5% $KHSO_4$ (3 × 20 ml), water (20 ml), dried with sodium sulphate, and filtered. The solvent was removed under reduced pressure to obtain the product as a viscous oil with the characteristic –NC stretching frequency at 2155 cm^{-1}. On storage in the refrigerator, the intensity of the –NC absorption decreased (as compared with that of the C=O) to ~60% after one year.

General procedure for dehydration of formamido polymers

The formamido polymer (50 mg–5 g) was fully swollen in pyridine for about 10 min, followed by addition of tosyl chloride (0.5 g per ml pyridine) in one portion. The mixture was vigorously stirred (or mixed with a spatula) during the addition, and it was cooled in an ice bath if the temperature rose to more than about 30°C. The gradual development of a yellow-to-pink colour within 2–5 min indicated complete dehydration, but the mixture was allowed to stand with occasional mixing for 5–10 min for type 2 and 5 polymers and for 10–15 min for 1, 3–4. The reaction mixture was then diluted with excess acetone, filtered, washed with acetone (× 2), methanol (× 2), 7% $KHCO_3$ (× 2), water (× 2), acetone (× 4) and ether (× 3). The polymer was finally dried at room temperature in a vacuum desiccator over phosphorus pentoxide.

Styrene-based isocyano polymers (1a, 1b)

N-Formylaminoglycine or 6-(*N*-formylamino)hexanoic acid (~6 equiv. based on polymer OH groups) was dissolved in DCM (10 ml).The solution was stirred in an ice bath, dicyclohexylcarbodiimide (DCC, 3 equiv.) was added, and the stirring was continued for 20 min, followed by 1 h at room temperature. The precipitated dicyclohexylurea was removed by filtration, and the solution was added to the resin (1 g, see *Table 1*).

4-Dimethyl aminopyridine (50 mg) was added, and the reaction mixture was allowed to stand at room temperature for 24 h. The mixture was then treated with excess acetic anhydride and triethylamine, and kept at room temperature for another 2 h. The acylated resin was recovered by filtration, washed with DCM (×6) and ether (×4), and dried in a vacuum oven at 35°C. Dehydration of the resulting formamido polymers was carried out as described above.

Styrene-based isocyano polymer (1c)

This was prepared as described for **1a** and **1b**, except that 2 equiv. of *in situ* formed *N*-formylglycine-*N*-oxysuccinimide and 2 equiv. of triethylamine were used for acylation.

Dimethylacrylamide-based isocyano polymers (2)

The amino polymer (1 g) was treated with an excess of a formylating reagent composed of methanol, methyl formate and triethylamine (volume ratios 10:5:1). The reaction mixture was kept at room temperature for 2 h, and was then refluxed for 3 h. The ninhydrin test[30] indicated complete formylation under these conditions. The polymer was recovered by filtration, washing with ether (×6) and drying in a vacuum desiccator in the presence of phosphorus pentoxide. Dehydration was carried out according to the above general procedure.

Styrene–acrylate and styrene–acrylamide polymers (3, 4)

Trans-esterification and aminolysis of the activated resin (see *Scheme 3*) were carried out by appropriate modifications of the general procedures described previously[24].

Dimethylacrylamide–acrylate isocyano polymers (5)

The formamido precursors of these polymers were prepared by water-in-oil suspension copolymerization of the monomers **6–8**, according to a previously published procedure[22]; and they were dehydrated as described above.

ACKNOWLEDGEMENTS

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