Synthesis, Reduction, and Subsequent Chemical Modification of Poly(methacrylonitrile) Based Resins

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A range of novel suspension polymerized resins based on poly(methacrylonitrile) have been synthesised, reduced using $LiAlH_4$, and further modified *via* reaction of the so-formed aminomethyl pendant group.

The use of polymer-suppported reactions in organic synthesis is now an accepted methodology[1] and potential technical applications are currently under investigation. Further rapid exploitation would be possible if supports capable of withstanding more hostile chemical regimes could be developed.[2] Existing polymers with aliphatic hydrocarbon skeletons *e.g.* polypropylene and polyethylene would provide attractive advantages but these materials are not easily formed as spherical particles. In addition, such substrates have only low porosity and limited surface area and are not readily derivatized.

Poly(acrylonitrile) is generally made *via* emulsion[3] or solution[4] polymerization and although its polymerization in suspension has been recorded,[4] there does not appear to have been any systematic study of this, nor indeed of the suspension polymerization of methacrylonitrile. Certainly there is no precedent for the synthesis of particulate resins based upon the latter monomer. We have now prepared a new range of crosslinked rigid spherical particulate resins of this type. Furthermore the nitrile function has proved readily reducible to yield, indirectly, resins formally derived from 2-methylallylamine, equation (1). In these not only is the amino group

$$-[CH_2C(Me)(CN)-]_n \xrightarrow{LiAlH_4} -[CH_2C(Me)(CH_2NH_2)-]_n \quad (1)$$

associated with a relatively inert aliphatic hydrocarbon segment, but this functionality readily provides convenient sites for further chemical modification. Appropriate adjustment to the composition of the monomer phase of suspension polymerizations also allows a variety of polymer morphologies to be generated, ranging from gel-type to macroreticular species.[5a] Supports with a wide range of porosities and surface areas are therefore readily available.

Suspension polymerizations were carried out as previously reported,[5b] though in the present work Biozan Gum R (Hercules Powder Co. Ltd., 0.3% w/v aqueous solution) was the stabiliser employed. In selecting suitable porogens for the formulation of macroreticular resins organic solvents which are precipitants (*i.e.* 'bad' solvents) for each particular copolymer composition are required. Commercial divinylbenzene consists of 50 vol.% of divinylbenzene isomers, the remainder being ethylstyrene isomers. Crosslink ratios are normally quoted as nominal vol.% of divinylbenzene in the comonomer mixture. Hence a 20% crosslinked resin contains 40 vol.% styrene residues and a 10% crosslinked species 20 vol.% styrene residues in the comonomer mixtures. Thus to select suitable precipitants for 10 and 20% crosslinked resins, the solubility characteristics of linear copolymers of methacrylonitrile made from 20 and 40 vol.% styrene mixtures were examined. The results in Table 1 indicate that toluene and cyclohexane are suitable precipitating porogens for a 10% crosslinked resin, and that cyclohexane and a mixture of cyclohexane/cyclohexanone (3/1 v/v) are suitable for a 20% crosslinked species. Table 2 shows the monomer phase compositions used in the suspension polymerizations along with the characteristics of the resulting resins. All of the reactions gave high yields of beaded products typically with an average diameter of *ca.* 400 μm. Resin 1 appears smooth and translucent and behaves essentially as a gel-type species, though in fact methacrylonitrile monomer is a precipitant for its own homopolymer. The resin absorbs only the thermodynamically 'good' solvent cyclohexanone. Resin 2 is a hybrid species since the porogen employed is a non-precipitating one. The dry product is smooth and opalescent and again only cyclohexanone is significantly imbibed. Resin 3 is another hybrid species readily absorbing both cyclohexanone and toluene (which is now also a 'good' solvent for this copolymer composition). Resins 4—7 are all white and opaque with a matt finish, and superficially appear typically macroreticular. Each absorbs both 'good' and 'bad' solvents, confirming the presence of macropores, and each even displays a significant up-take of water.

Examination of the literature surprisingly revealed no obvious references to the reduction of nitrile polymers using $LiAlH_4$, although a reduction using H_2 and Raney Nickel is reported.[6] Our resins were readily reduced by refluxing in suspension with an excess of $LiAlH_4$ in tetrahydrofuran (THF) typically for 48 h. Beads were collected and washed with ethyl acetate (to destroy excess of $LiAlH_4$), hydrochloric acid (2 M), sodium hydroxide (2 M), water, and acetone, before vacuum drying. I.r. spectra (Nujol) showed virtually complete loss of the the $C\equiv N$ stretch at *ca.* 2200 cm^{-1} and the appearance of a broad N–H stretch at *ca.* 3400 cm^{-1}. Reductions using $BH_3\cdot THF$ were significantly less effective with a significant residual $C\equiv N$ absorption band always appearing in the spectra of treated resins. Elemental microanalyses [*e.g.* for Resin 4 reduced with $LiAlH_4$, found (%): C, 46.3; H, 5.6; N, 5.2; calc. (%) for complete reduction of a 40% styrene/methacrylonitrile copolymer: C, 79.8; H, 12.4; N, 10.0] indicated the presence of substantial amounts of trapped inorganic residues (Al, Li oxides?), which was confirmed by quantitative combustion of a larger sample in a muffle furnace at 825 °C (23% residue for above example). Treatment of reduced resins with concentrated nitric acid at room tempera-

Table 1. Solubility characteristics of methacrylonitrile, poly(methacrylonitrile), and copolymers with styrene.

	Methacrylonitrile		Copolymer	
Solvent	Monomer	Homo-polymer	20 vol.% Styrene	40 vol.% Styrene
Toluene	Y[a]	N	N	Y
Cyclohexanone	Y	Y	Y	Y
Acetonitrile	Y	Y	Y	Y
Cyclohexane	Y	N	N	N
Cyclohexane/ cyclohexanone (3/1, v/v)	Y	—	—	N

[a] Y = soluble, N = insoluble.

Table 2. Suspension polymerization monomer phase compositions and resulting resin characteristics.

					Solvent up-take by resins (g/g)			
Resin	Crosslink ratio[a]	Porogen	Ratio porogen comonomers (v/v)	Resin type[b]	Cyclohexanone	Toluene	Cyclohexane	Water
1	4	—	—	Gel	0.52	0.02	0.06	0.03
2	10	Cyclohexanone	7/3	Hybrid	0.75	0.03	0.28	0.03
3	20	Toluene	3/2	Hybrid	1.20	0.79	0.23	0.08
4	20	Cyclohexane	1/1	Macrorecticular	1.59	1.63	0.97	0.10
5	20	Cyclohexane	2/1	Macroreticular	1.93	2.63	1.30	0.19
6	20	Cyclohexane/ cyclohexanone (3/1, v/v)	1/1	Macroreticular	1.19	1.16	0.68	0.12
7	20	Cyclohexane/ cyclohexanone (3/1, v/v)	2/1	Macroreticular	2.06	2.18	0.50	0.10

[a] Nominal value = 0.5 × % commercial divinylbenzene used. [b] Spherical particles *ca.* 400 μm av. diameter.

ture for 12 h followed by neutralization with sodium hydroxide (5 M) for a similar period removed a large amount of this residue, although some appeared to be held tenaciously by the resin [for above example after acid/alkali treatment, found (%): C,70.7; H,8.0; N,7.6].

Despite the residual inorganic contaminant subsequent further chemical modification of the amino function (originally Resin 4) *via* reaction with (a) iodomethane in refluxing acetone, (b) 5 M HCl at room temperature, and (c) *o*-chlorobenzoyl chloride/pyridine under reflux, proved to be readily achieved, yielding resins containing 8.0% I, 11.8% Cl, and 12.7% Cl respectively.

The synthesis of crosslinked poly(methacrylonitrile) based resin beads can be achieved in good yield and with considerable morphological variation. Reduction of the nitrile function to an aminomethyl group is easy, and we believe the resulting materials have considerable potential for application as supports with improved stability and yet ease of derivatization.

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References

1 A. Akelah and D. C. Sherrington, *Polymer*, 1983, **24**, 1369.

2 J. Klein and H. Widdecke, *Erdoel Kohle, Erdgas, Petrochem. Brennst. Chem.*, 1983, **36**, 307.

3 C. E. Schildknecht, in 'Vinyl and Related Polymers,' Wiley, New York, 1952, ch. V, p. 263.

4 K. J. Saunders, in 'Organic Polymer Chemistry,' Chapman and Hall, London, 1973, ch. 6, p. 131.

5 D. C. Sherrington, in 'Polymer-supported Reactions in Organic Synthesis,' eds. P. Hodge and D. C. Sherrington, Wiley, London, 1981, (a) ch. 1, p. 16; (b) appendix.

6 W. H. Schuller and L. C. Beegle, American Cyanamid Co., U.S. Pat. 3 122 526/1964.