Separation of Polymer from a Matrix Polymerized Complex of Ionene-poly(vinyl sulphonate)

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Summary Poly(vinyl sulphonate) prepared on a polycationic matrix of low molecular weight has been successfully separated and studied; it has a low molecular weight analogous to the molecular weight of the matrix and is characterized by a specific interaction pattern with the original matrix.

We have recently shown that the free-radical-initiated polymerization of p-styrenesulphonic acid attached to a polycationic macromolecule proceeds at rates over 3 orders of magnitude higher than the rate of polymerization of an aqueous solution of the sodium salt of p-styrenesulphonic acid.[1] Polymerization on the polycationic matrix was also

found to proceed with lower overall activation energy and the rate law suggested a monomolecular termination of chain propagation, possibly through chain transfer.[1]
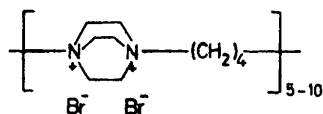
(1)

We now report the separation of poly(vinyl sulphonic acid), in the form of its sodium salt, from a polycationic matrix identical to the one previously described.[1] The matrix is obtained by step-growth addition of 1,4-diazabicyclo[2,2,2]-octane and 1,4-dibromobutane, and is the quaternary

matrix were identical. The separation yield was 50% (amount of polymer separated/amount of monomer initially present).

The intrinsic viscosities listed in the Table were measured in 0·1M aqueous sodium sulphate at 25°. Plots of $1/\eta_{red}$ vs. $c^{1/2}$ gave straight lines with positive slopes. In view of the low molecular weight of the investigated polymers no correction for shear dependence was made. The molecular weights $\overline{M}_n$ were calculated from values of $[\eta]$ using data of Breslow and Kutner.[3] It is probable that for both low molecular weight polymers, the molecular weight $\overline{M}_n$ is overestimated by 10—20%.

The Table shows that the intrinsic viscosity of the matrix prepared polymer is very low, due to the low molecular weight of the matrix.[1] When the separated polymer is

TABLE

	Intrinsic viscosity $[\eta]/dl\ g^{-1}$	$\overline{M}_n$	Crystallinity of polymer (X-ray)	Crystallinity of complex obtained by mixing the polymer with matrix
Matrix polymerized polymer	0·04	5000	None detected	Bands at: 4·4 Å (b,m); 5 Å (b,w); 5·6 Å (s,m); 9·8 Å (s,i)
Reference polymer (I)	0·26	34500	None detected	Bands at 4·4 Å (b,vw); 12 Å (b,vw)
Reference polymer (II)	0·04	5000	None detected	Bands at 5·6 Å (b,w); 9·8 Å (b,m). Halo at ca. 7·0 Å

ammonium polyelectrolyte ionene bromide (1). An aqueous solution of ionene bromide is first converted into ionene hydroxide and then neutralized with an equivalent amount of vinylsulphonic acid. The complex is then polymerized in water using 4,4'-azobis-4-cyanovaleric acid. The polymerized complex precipitates and is dissolved in concentrated hydrochloric acid. The ionene matrix is then separated by precipitation with potassium persulphate. The solution contains the poly(vinyl sulphonic acid) sodium salt. It is subjected to ultrafiltration, using a membrane (Amicon UM-05) with a cut-off molecular weight of 500. The solution containing the polymer free from all low molecular weight impurities is freeze-dried and the polymer recovered.

Two reference polymers were prepared by solution polymerization.[2] Elemental analysis of the separated polymer was satisfactory and the i.r. spectra of the two reference polymers and the polymer separated from the

mixed with the matrix in water it gives an insoluble complex which after drying shows a powder X-ray pattern with 4 distinctive bands, 2 sharp and 1 broad of relatively high intensity. The reference polymer (I), of higher molecular weight gives two broad and weak bands whereas the low molecular weight reference polymer (II) gives 2 broad bands and a halo (Table). Thus, the reference polymers complexed with the matrix seem to be less organized than the polymer prepared on the matrix, separated and brought back into contact with the matrix. This points towards a specific interaction pattern between the matrix synthesized polymer and the matrix, possibly due to an enhancement in stereoregularity of the polymer.

[1] A. Blumstein, S. R. Kakivaya, K. R. Shah, and D. J. Wilkins, J. Polymer Sci., Part C, Polymer Symposia, Symposium on Polyelectrolytes, Chicago, 1973 (in the press).
[2] D. S. Breslow and G. E. Hulse, J. Amer. Chem. Soc., 1954, 76, 6399.
[3] D. S. Breslow and A. Kutner, J. Polymer Sci., 1958, 27, 295.