

Preparation of potentially electroactive thallium polymers derived from the acidic copolymers of maleic anhydride

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Maleic anhydride copolymers with vinyl ethyl ether and *N*-vinyl-2-pyrrolidone were prepared in tetrahydrofuran at 60°C, using AIBN as initiator. Copoly (MA-VEE) was hydrolysed to various degrees of hydrolysis and the extent of hydrolysis monitored by i.r. Various acidic derivatives of copoly(MA-VEE), copoly(MA-*N*-vinyl-2-pyrrolidone) and copoly(MA-ethylene) were prepared and characterized by elemental analysis and spectroscopy. The inter- and intramolecular crosslinking of carboxylic groups in copoly(succinic acid-VEE) were studied by g.p.c. Also thallium (III) derivatives of several acidic polymers were prepared and characterized.

Keywords Maleic anhydride; copolymers; vinyl ethyl ether; thallium; vinyl pyrrolidone; electroactive

INTRODUCTION

Copolymers of maleic anhydride (MA) with vinyl monomers have been studied extensively owing to their potential applications as polyelectrolytes¹. Copolymers of MA and divinyl ether have been found useful for medical applications due to their relatively high biocompatibility². Hydrolysed copolymers of MA have been used as model compounds for studying the intermolecular hydrophobic interactions which may be related to natural polyelectrolytes as proteins³. The interactions between the carboxylate groups in these electrolytes with the counterions have been studied particularly since the high charge density on the polymeric ion exerts a strong electrostatic force⁴. It has been reported⁵ that the chelation of alkaline earth cations by the bidentate ligands of these polymers offers certain advantages, since the number of ligands bound by the chelating ions is more certain. The dissociation of these electrolytes is comparable to that of analogous succinic acid chelates⁵.

Thallium (I) and thallium (III) carboxylates are generally known to catalyse a number of industrially important aromatic substitutions⁶. The chelating ability of these acidic polymers, together with the relatively high stability constants of thallium (III) derivatives^{7,8} suggests the possibility of incorporating thallium (I) and thallium (III) into acidic polymers derived from MA copolymers. In analogy with low molecular weight thallium derivatives, the thallium containing polymers may also be catalytically active and their use for the preparation of surface-modified electrodes⁹ is particularly interesting.

The majority of the above mentioned acidic polymers have been obtained by simple hydrolysis of the corresponding anhydride polymers. This route provides adjacent groups on the polymer which are particularly interesting as bidentate ligands. More recently, we have briefly described the conversion of crosslinked copolymers of MA to a wide range of acidic derivatives by

reacting the anhydride polymer with various nucleophiles such as alcohols, phenol, amines and amino acids¹¹. Thus, the preparation of a series of soluble acidic polymers from copolymers of MA with ethylene, vinyl ethyl ether, and *N*-vinyl-2-pyrrolidone, respectively is reported here. Thallium (III) derivatives of the acidic polymers were also prepared in bulk or on electrode surfaces. The work concerning the electrochemical characterization and application of the thallium containing polymers will be published later.

EXPERIMENTAL

Materials

Maleic anhydride (GPR, BDH) was recrystallized twice from chloroform (m.p. 63°C). Vinyl ethyl ether (AR, BDH) was washed with water, dried over KOH pellets (overnight) and finally distilled over sodium metal (b.p. 35–36°C). *N*-Vinyl-2-pyrrolidone (Aldrich) was distilled before use, (b.p. 70°C, 0.5 mm Hg). 2,2'-azo-bis-(2-methylpropionitrile) (AIBN) was recrystallized from chloroform and dried *in vacuo* at room temperature. Tetrahydrofuran (THF) (GPR, BDH) was refluxed over calcium hydride (overnight) and then distilled over fresh calcium hydride. Copoly(ethylene-maleic anhydride) was used as received from Aldrich. Thallium trifluoroacetate (technical), diethylamine, aminoethyl sulphonic acid (Taurine), and benzylamine were obtained from Aldrich and used without further purification.

Polymer characterization

The weight average molecular weight (\bar{M}_w) and the number average molecular weight (\bar{M}_n) were determined by gel permeation chromatography. Tetrahydrofuran with 1% 2,6-di-*tert*-butyl-*p*-cresol was used as eluent at the flow rate of 1 cm³ min⁻¹. Polystyrene samples were used as calibration standards.

I.r. spectra were recorded in Nujol on a Perkin-Elmer 298 spectrophotometer. ^{13}C n.m.r. spectra were recorded on a Bruker WH-250 spectrometer operating at 62.9 MHz in the pulsed Fourier transform mode, with decoupling from protons by broad band irradiation. The free induction decay was recorded at 16K points. For solutions in CDCl_3 and/or d_6 -DMSO, chemical shifts were measured with reference to TMS.

Thallium analyses were performed at Rooney Laboratories Ltd. (Surrey, England).

Preparation of copoly(maleic anhydride-vinyl ethyl ether) (1a)

Vinyl ethyl ether (6.76 cm^3 , 0.125M), maleic anhydride (12.25 g, 0.125M), and AIBN (0.2 g) were dissolved in tetrahydrofuran (110 cm^3) contained in a 3-necked flask fitted with a thermometer, nitrogen inlet, magnetic stirrer, and a condenser. The flask was heated in an oil bath at 60°C (internal temperature). The polymerization was allowed to continue for 3½ h, followed by precipitation of the copolymer by pouring the THF solution into excess ether. The polymer was again dissolved in THF, reprecipitated in ether, washed with ether, and finally dried under vacuum at room temperature, to obtain the final product, 14.1 g (74%).

Preparation of copoly(maleic anhydride-N-vinyl-2-pyrrolidone) (2a)

MA (9.8 g, 0.1M) and N-vinyl-2-pyrrolidone (11.12 g, 0.1 M) were dissolved in THF (100 cm^3). The solution was flushed with argon and AIBN (0.20 g) was added. The polymerization was carried out in a water bath at 60°C for 3.5 h. The reaction mixture was diluted with THF (40 cm^3) and the polymer was then precipitated into excess ether. The polymer was redissolved and then reprecipitated into ether and dried under vacuum, 17.9 g (86%).

Preparation of copoly (succinic acid-vinyl ethyl ether) (1b)

1a (30 g) was refluxed in water (120 cm^3) for about 8 h. The solution was then cooled to room temperature, mixed with dimethylformamide (50 cm^3), and the solvent was evaporated under reduced pressure. The residual water in the polymer was mostly removed by twice dissolving the polymer in dioxane (150 cm^3) followed by evaporation of the solvent. The polymer was again dissolved in dioxane (150 cm^3) and precipitated in ether, filtered, and dried *in vacuo*, 28 g (84%).

Preparation of copoly (succinic acid-N-vinyl-2-pyrrolidone) (2b) and copoly (succinic acid-ethylene) (3b)

These were prepared by refluxing the corresponding maleic anhydride copolymers 2a (1 g) and 3a (1 g) with water: THF (3:1) (4 cm^3) for 3.5 h, and 5 h, respectively. Further processing of the polymer was performed as described in the preparation of 1b.

Preparation of the half-methyl ester of 1a (1c)

A mixture of the anhydride polymer 1a (6 g) and methanol (300 cm^3) was refluxed for 24 h. The polymer was precipitated into excess 2M HCl and was subsequently reprecipitated from THF solution into 2M HCl, and then dried under vacuum, 5.46 g (77%).

Preparation of half-N-benzylsuccinimide derivative of 1a (1d)

Benzylamine (0.54 g, 5 mmole) in dioxane (10 cm^3) was added with vigorous stirring at room temperature to the solution of maleic anhydride polymer 1a (1.7 g, 10 m mole copolymer repeat unit) in dioxane (34 cm^3). The reaction mixture was then concentrated to 10 cm^3 and refluxed for 3 h. The solution was cooled to room temperature and the solvent was then evaporated completely. The residual polymer was dissolved in chlorobenzene (10 cm^3) and precipitated into a large excess of ether, filtered and dried *in vacuo*, 1.89 g (92%).

The corresponding acid polymer (1e) was prepared by heating the anhydride 1d (0.5 g) in water (2 cm^3) at 50°C for about 12 h.

Preparation of half-diethylamide derivative of 2a (2f)

To a solution of the anhydride polymer 2a (2 g) in dimethylformamide (15 cm^3) was added diethylamine (0.5 cm^3). A white precipitate formed almost immediately, and the mixture was stirred for 1 h at room temperature. The solvent was evaporated (two coevaporations with water), and the precipitate was dissolved in 0.1M sodium hydroxide. The solution was then acidified with 1M hydrochloric acid (15 cm^3). The polymer was then filtered, washed with 1 M hydrochloric acid (twice, 10 cm^3) and finally dried under vacuum, 1.7 g (63%).

Preparation of copoly[ethylene-N-(2-sulphonic acid-ethane succinimide)] (3g)

A mixture of poly(ethylene-maleic anhydride) (6.3 g, 0.15 mole) and 2-amino-sulphonic acid (taurine, 12.5 g, 0.10 mole) were stirred in dimethylformamide (50 cm^3) at 130°C for 4 h. The reaction mixture was cooled to room temperature, filtered, and the solution was added dropwise to excess ethylacetate. The coagulated polymer was dissolved in methanol, and precipitated into excess ethyl acetate. The precipitate was filtered off, and stirred in ether for 30 min, before being finally filtered and dried to constant weight under vacuum. The yield was quantitative.

Preparation of thallium (III) derivatives of acidic polymers

Thallium derivatives were prepared by dropwise addition of a solution of Tl (III) trifluoroacetate in water-THF (see Table 2) to the solution of the appropriate polymer in the same solvent mixture while stirring vigorously. The mixture was then stirred for 10 min, before the precipitate produced was filtered, then washed with the same solvent mixture, and dried under vacuum. Further details of the preparation and yields of the thallium derivatives are presented in Table 1.

RESULTS AND DISCUSSION

Molecular weights and hydrolysis of copoly(MA-VEE)

The weight average molecular weight (\bar{M}_w) and the dispersity indices, (\bar{M}_w/\bar{M}_n), of different polymers are presented in Table 2. It is particularly interesting to note that the hydrolysis of anhydride polymer 1a to give 1b is accompanied by a considerable decrease in the molecular weight of the polymer. This phenomenon has also been reported by previous workers¹², but no explanation has been given. Slight variations of molecular weight may arise from the changes in the chemical structure of the

Table 1 Preparation^a of thallium (III) derivatives of acidic polymers

Polymer	Polymer unit formula	Polymer concentration (mg/cm ³)	Solvent ^b water THF (v/v)	Yield ^c (%)	Elemental analysis						Solubility of Tl(III) Polymer ^d						
					C		H		N		Tl		H ₂ O	THF	DMF		
					calcd	found	calcd	found	calcd	found	calcd	found					
1b	C ₁₀ H ₁₀ O ₇ F ₃ Tl	10	1:1	97(VIII)	23.86	25.42	1.99	2.75	—	—	—	—	—	—	—	—	—
	C ₁₈ H ₂₀ O ₁₂ F ₃ Tl	—	—	71(IX)	31.26	32.81	2.89	3.13	—	—	—	—	—	—	—	—	—
1b^e	C ₁₈ H ₂₀ O ₁₁ F ₃ Tl	10	1:3	82(VIII)	32.10	32.81	2.97	3.13	—	—	—	—	—	—	—	—	—
1c	C ₁₀ H ₂₄ O ₁₂ F ₃ Tl	20	1:2	98(X)	16.74	17.23	3.35	3.61	—	—	—	—	—	—	—	—	—
1e	C ₂₅ H ₂₇ O ₁₀ F ₃ NTl	5	1:1	76(VIII)	39.37	39.12	3.54	3.54	1.84	2.06	—	—	—	—	—	—	—
2b	C ₁₂ H ₁₁ O ₇ NF ₃ Tl	10	1:1	80(VIII)	26.57	29.68	2.03	2.24	2.58	2.97	—	—	—	—	—	—	—
	C ₂₂ H ₂₄ O ₁₂ F ₃ N ₂ Tl	—	—	56(IX)	34.33	29.68	3.12	2.24	3.64	2.97	—	—	—	—	—	—	—
3e	C ₁₈ H ₂₀ O ₁₂ N ₂ S ₂ F ₃ Tl	25	1:1	71(XI)	27.66	28.42	2.56	2.95	3.59	28.42	—	—	—	—	—	—	—

^a 20 mg/cm³ of thallium (III) trifluoroacetate in water-THF^b was added to the stirred polymer solution

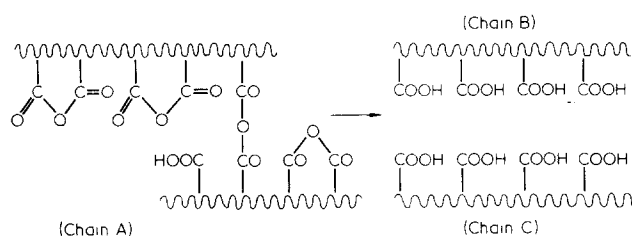
^b Ratio of water: THF was chosen to keep the reactants in a homogeneous solution

^c Yields are calculated based on the speculated molecular formula and the type of thallium polymer which is given in brackets

^d (+) completely soluble; (—) partly soluble/insoluble

^e 45–50% carboxylic groups present in the polymer based on the semi-quantitative i.r. analysis

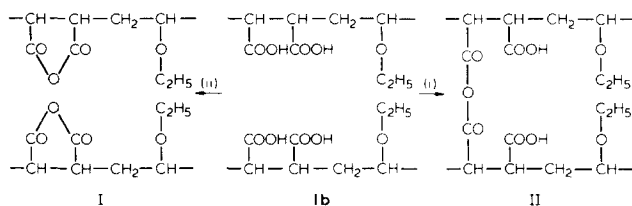
polymer (i.e., **1a**→**1b**), but we suspected that the approximate four fold molecular weight decrease may be explained by the following reaction:



Scheme 1

The inter-polymeric anhydride (chain A) could be formed, during the copolymerization, by thermal dehydration of any acidic -COOH groups that may have originated from acidic impurities, such as maleic acid, which was subsequently copolymerized, or by slight unavoidable hydrolysis of maleic anhydride units in the copolymers. Alternatively, a transfer reaction between the anhydride groups of different polymeric chains might have occurred. Similar reactions are also known to lead to polymer crosslinking in the copolymerization of MA and vinyl acetate¹³. These observations were further confirmed by the attempted conversion of the acidic polymer (**1b**) to the initial anhydride polymer (**1a**) according to scheme 2. It was observed that although the formation of five membered ring anhydride was significantly favoured, the alternate inter-chain anhydride formation also took place, to an extent depending on the precise experimental conditions.

Two experiments were carried out using 1.25% (w/v) and 25% (w/v) polymer solutions of **1b** in dioxane. The polymer solution was, in either case, refluxed at 100°C for 17 h, and the mixture was then kept at 120°C for 5 h, and subsequently the molecular weights of the isolated polymer samples were then measured by g.p.c. These molecular weights are compared with those of the initial anhydride (**1a**) and acidic polymers (**1b**) in Table 2. As can be seen from these results, in the case of the dilute solution, \bar{M}_w increased from 2550 to 11900 and the dispersity index from 1.61 to 2.03. The latter values of \bar{M}_w/\bar{M}_n are interestingly very similar to those of the initial anhydride polymer. For the concentrated solution, \bar{M}_w increased from 2550 to 29500 and the dispersity index from 1.61 to 3.05 which can again be explained by the intermolecular dehydration reaction shown in Scheme 2. However, we were not able to prepare insoluble anhydride polymers in other experiments by this way.



Scheme 2 (i) intermolecular process (ii) intramolecular process

Thus in the case of dilute solution, the formation of I is predominant, although some molecular containing structure such as II are also formed and the observed molecular weight increase is only four fold. But, in concentrated solution, the possibility of intermolecular anhydride

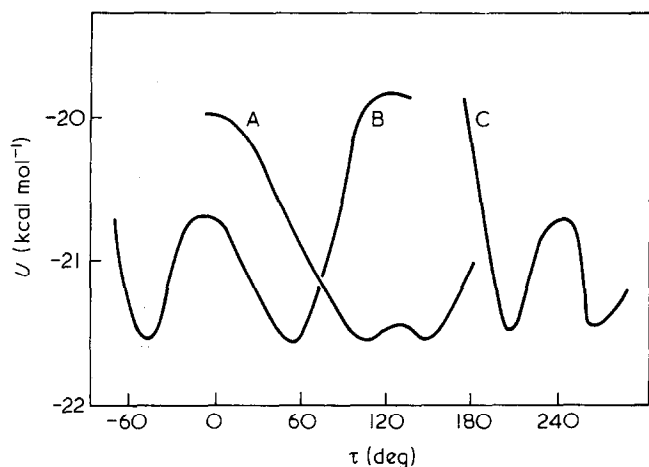


Figure 6 The energy barriers to $a_1 \rightarrow a_2$ and $a_1 \rightarrow a_3$ transitions. Curves A, B and C, correspond to variation of τ_2^2 ; τ_2 ; τ_3 respectively

The occurrence of 'soft' degrees of freedom and distinct conformational states makes model a_0 advantageous from the entropic point of view.

A comparison of model a_0 with model a_6 , an analogue of the models in refs. 5 and 9, shows that a_0 , while possessing an acceptable R'' -factor, is approximately 2 kcal mol^{-1} more stable. In principle, an energy of the order of $1\text{--}2 \text{ kcal mol}^{-1}$ is within the accuracy ensured by the atom-atom potential method in predictions of the absolute values of the lattice energy. Nevertheless, the 2 kcal mol^{-1} difference between a_0 and a_6 appears to be quite significant. It is apparent that the errors introduced to the lattice energy by assumptions and approximations of the atom-atom potential method are generally systematic and, as a consequence, greatly cancel out in computing the energy difference between different modifications of the same crystal. This has been demonstrated, for instance, by Bernstein and Hagler²³ for polymorphic modifications of *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline.

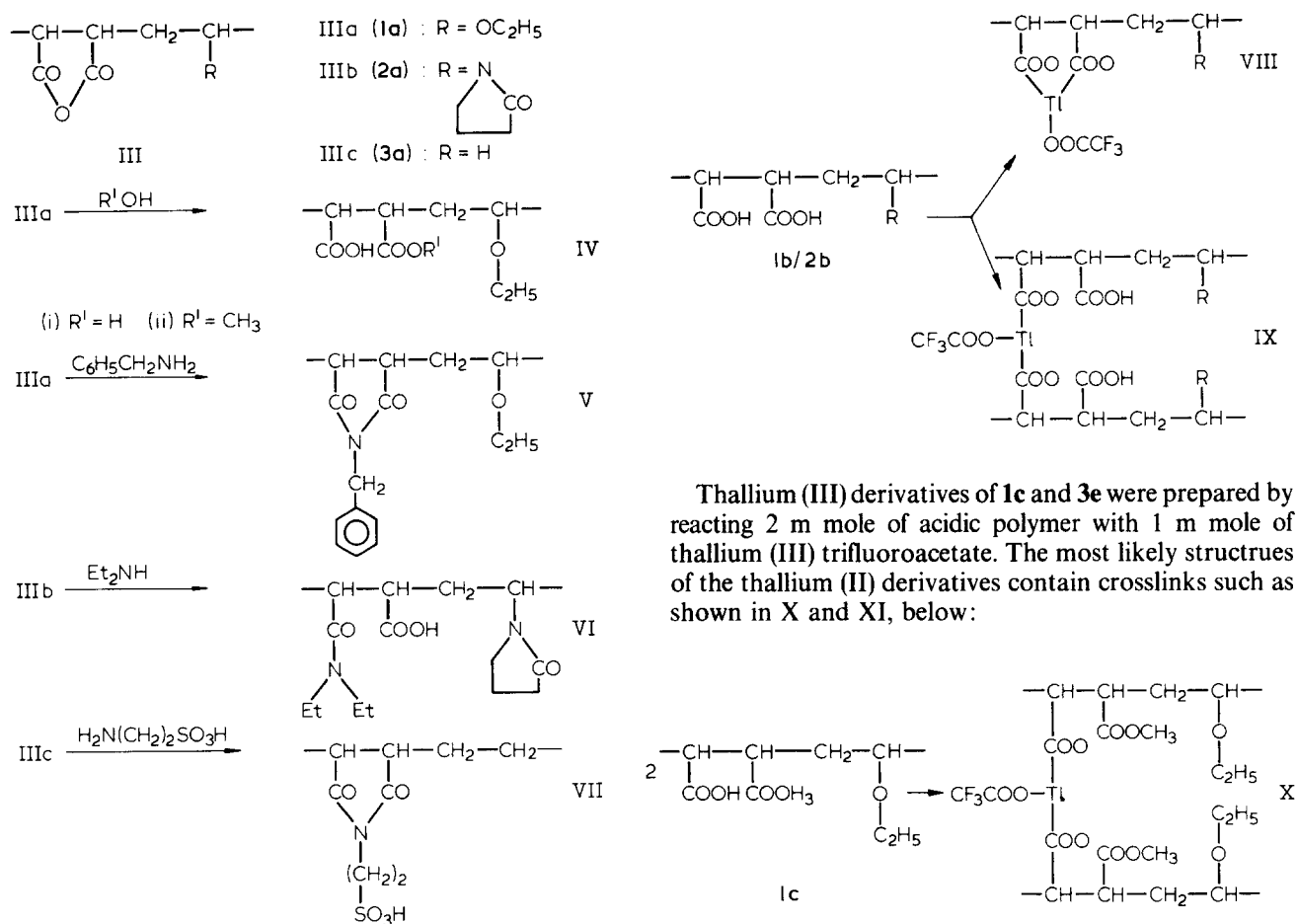
One further argument in favour of model a_0 over a_6 is provided by comparison of the structure amplitudes for 002 and 004 meridional reflections. Due to the known difficulties in applying Lorentz and polarization corrections to the meridional reflections, their intensities have not been estimated quantitatively⁶ and have not been included in the R'' -factor. Visually, these reflections are observed as moderately weak and strong, respectively, which qualitatively agrees with model a_0 ($|F_{002}|/|F_{004}| = 1.5/26.3$) and conflicts with a_6 ($|F_{002}|/|F_{004}| = 27.8/21.8$).

CONCLUSIONS

The detailed scanning of the configurational space of a 16-parameter model of mercerized cellulose has revealed a variety of structures consistent with the available X-ray diffraction data. The use of an additional, energetic criterion, based on the atom-atom approximation to the potential energy, has allowed one antiparallel model (a_0) to be selected as the most probable. The remarkable feature of this model is the ability of its hydrogen bonding network to undergo facile rearrangement through thermal migration of protons. Although the available experimental data are too few to substantiate the optimum model in full detail, the success of the atom-atom potential method in describing the structure and properties of organic crystals supports the predicted structure.

REFERENCES

- 1 Sarko, A. and Muggli, R. *Macromolecules* 1974, 7, 486
- 2 Woodcock, C. and Sarko, A. *Macromolecules* 1980, 13, 1183
- 3 Gardner, K. H. and Blackwell, J. *Biopolymers* 1974, 13, 1975
- 4 French, A. D. *Carbohydr. Res.* 1978, 61, 67
- 5 Kolpak, F. J. and Blackwell, J. *Macromolecules* 1976, 9, 273
- 6 Kolpak, F. J., Weih, M. and Blackwell, J. *Polymer* 1978, 19, 123
- 7 Jones, D. W. *J. Polym. Sci.* 1960, 42, 173
- 8 Watanabe, S. and Hayashi, J. *Kogyo Kagaku Zasshi* 1970, 73, 1890
- 9 Stipanovic, A. and Sarko, A. *Macromolecules* 1976, 9, 851
- 10 Hunter, R. E. and Dweltz, N. E. *J. Appl. Polym. Sci.* 1979, 23, 249
- 11 Blackwell, J. and Marchessault, R. H. in 'Cellulose and Cellulose Derivatives' (Eds. Bikales, N. M. and Segal, L.) Part IV, Wiley, N.Y., London, Sydney, Toronto, 1971
- 12 Kitaigorodsky, A. I. 'Molecular Crystals and Molecules', Academic Press, N.Y., London, 1973
- 13 Arnott, S. and Scott, W. E. *J. Chem. Soc., Perkin Trans. II* 1972, 2, 324
- 14 Pertsin, A. J., Nugmanov, O. K., Sopin, V. F., Marchenko, G. N. and Kitaigorodsky, A. I. *Vysokomol. soed.* 1981, 23(A), 2147
- 15 Zugenmaier, P. and Sarko, A. in 'Fiber Diffraction Methods', Am. Chem. Soc. Symp. Ser. No. 141, 1980, 226
- 16 Legrand, C. *Acta Crystallog.* 1952, 5, 800
- 17 Norman, N. *Textile Res. J.* 1963, 33, 711
- 18 Dashevsky, V. G. 'Konformatsii organicheskikh molekul' (in Russian), Khimia, Moscow, 1974
- 19 Mirskaya, K. V., Kozlova, I. E. and Bereznitskaya, V. F. *Phys. Stat. Sol.* 1974, 62, 291
- 20 Kitaigorodsky, A. I., Mirskaya, K. V. and Nauchitel', V. V. *Kristallografia* 1969, 14, 900
- 21 Hamilton, W. C. *Acta Crystallogr.* 1965, 18, 502
- 22 Powell, M. J. D. *Computer J.* 1964, 7, 155
- 23 Newton, M. D., Jeffrey, G. A. and Takagi, S. *J. Am. Chem. Soc.* 1979, 101, 1997
- 24 Jeffrey, G. A. and Maluszynska, H. *Int. J. Quantum. Chem., Quantum Biol. Symp.* 1981, 8, 231
- 25 Bernstein, J. and Hagler, A. T. *J. Am. Chem. Soc.* 1978, 100, 673



Scheme 3

succinimido polymers V and VII were prepared by the reaction of anhydride polymer with ethylaminosulphonic acid (taurine) or benzylamine at 130°C for 4 h.

Some of the basic features of copolymers of anhydride with vinyl ethyl ether, *N*-vinyl-2-pyrrolidone, and ethylene, respectively, and a number of their derivatives are given in Table 3. The solubilities of these polymers in water, dimethylformamide, tetrahydrofuran and dichloromethane are also presented. Further, anhydride polymers and their derivatives were characterized by microanalysis and i.r. spectroscopy and some of this data is shown.

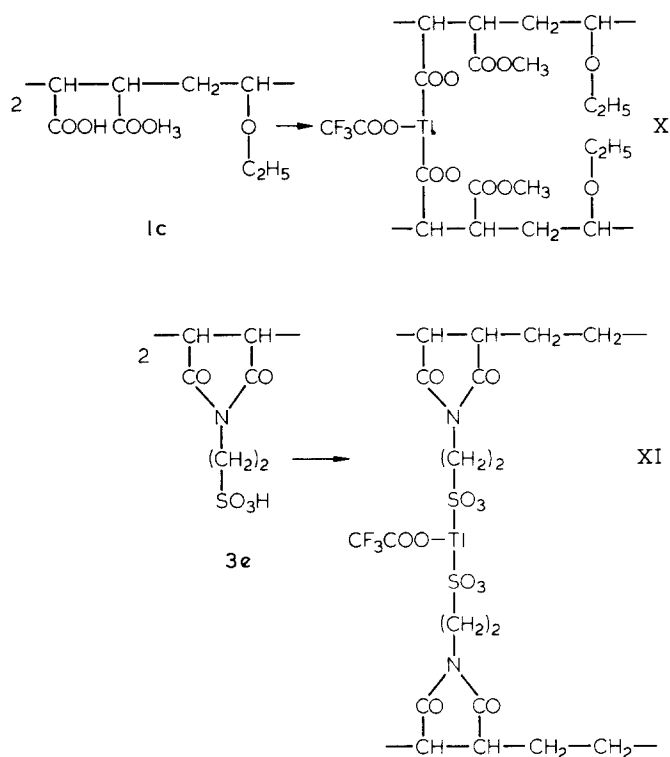
Maleic anhydride copolymers are suitable for the preparation of acidic polymers following various degrees of hydrolysis. Copoly (MA-VEE) (1a) was hydrolysed from 30% to 100% to give acidic polymers, depending on the experimental conditions. The % hydrolysis was estimated semi-quantitatively using i.r. spectroscopy.

Nature of thallium (III) derivatives of acidic polymers

Thallium (III) derivatives of copoly (succinic acid-VEE) (1b) and copoly (succinic acid-*N*-vinyl-2-pyrrolidone) (2b) were prepared by reacting 1 mmole of 1b/2b with 1 m mole of thallium (III) trifluoroacetate in a THF water mixture (see Table 1). The most likely structures of these thallium (III) derivatives, VIII and IX, are given below:

From the microanalysis, solubility and the reaction conditions (Table 1), it is suggested that the formation of VIII is favoured over IX, although other possibilities exist of forming Tl(III) derivatives within the same chain/with other chains¹⁰.

Thallium (III) derivatives of 1c and 3e were prepared by reacting 2 m mole of acidic polymer with 1 m mole of thallium (III) trifluoroacetate. The most likely structures of the thallium (III) derivatives contain crosslinks such as shown in X and XI, below:



Thus these Tl(III) derivatives were insoluble in water, DMF and THF, suggesting that the copolymer derivatives were intermolecularly crosslinked as indicated.

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REFERENCES

- 1 Bianchi, E., Ciferri, A., Paradi, R., Rampone, R. and Teardi, A. *J. Phys. Chem.* 1970, **74**, 1050; Dubin, P. L. and Strauss, U. P. *J. Phys. Chem.* 1970, **74**, 2842; 1973, **77**, 1427
- 2 Umrigar, P., Hashi, S. and Butler, G. B. *J. Polym. Sci., Polym. Chem. Edn.* 1979, **17**, 351
- 3 Ohno, N., Nitta, K., Makino, S. and Sugai, S. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 413
- 4 Quadrifoglio, F., Crescenzi, V. and Delbin, F. *Macromolecules* 1973, **6**, 301; Delbin, F., Paoletti, S., Crescenzi, V. and Quadrifoglio, F. *Macromolecules* 1974, **7**, 538
- 5 Martell, A. E. and Calvin, M. 'Chemistry of the metal chelate Compounds', Prentice Hall Inc., New York, 1952, p. 517
- 6 McKillop, A., Fowler, J. S., Zelesko, M. J., Hunt, J. D. and Taylor, E. C. *Tetrahedron Lett.* 1969, 2423; McKillop, A. and Taylor, E. C. *Adv. Organometal. Chem.* 1973, **11**, 165
- 7 McKillop, A., Hunt, J. D. and Taylor, E. C. *J. Organomet Chem.* 1970, **24**, 77; McKillop, A. and Taylor, E. C. *Adv. Organometal. Chem.* 1973, **11**, 164
- 8 Lee, A. G. in 'Organometallic Reactions', Eds. E. L. Becker and M. Tsutsui, Wiley-Interscience, N.Y., 1975, Ch. 5, p. 1
- 9 Albery, W. J. and Hillman, A. R. *Ann. Reports C., Roy. Soc. Chem.* 1981, **78**, 377
- 10 Lee, A. G. *J. Organometal Chem.* 1970, **22**, 537
- 11 Arshady, R. *Polymer* 1982, **23**, 947
- 12 Shimizu, T., Minakata, A. and Tomiyama, T. *Polymer* 1980, **21**, 1427
- 13 Arshady, R., unpublished observations