

PERFLUOROSULPHONATED POLYMERS AS NEW MATERIALS FOR IR SPECTROSCOPY

Alexandr JEGOROV^a, Miroslav EBERT^a, Jan WEBER^b and Pavel JANDA^b

^a Department of Inorganic Chemistry, Charles University, 128 40 Prague 2 and

^b J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, U továren 254, 102 00 Prague 10

Received January 29th, 1986

Thin films of perfluorosulphonated polymer were obtained by dissolving a Nafion 117 membrane in N,N-dimethylacetamide or hexamethylphosphoric triamide and subsequent evaporation of the solution. These films can be used as a medium for IR spectroscopy in the range $4\,000-1\,300\text{ cm}^{-1}$, suitable for retention and identification of cations. Spectra of cations in polymer cationic forms (NH_4^+ , $\text{Me}_n\text{NH}_3^{+n}$, $\text{Et}_n\text{NH}_3^{+n}$) and of some allylammonium cations were studied.

Perfluorosulphonated polymers, mostly known by the name Nafion (Du Pont), are widely applied as membranes for electrolysis, as ion exchangers, catalysts or electrode modifiers. In spite of the large number of application possibilities, very few papers have been devoted to studies of the infrared spectra of these polymers¹⁻³. The cited papers were mostly devoted to investigations of the bands assigned to the polymer backbone of Nafion membranes in H^+ form or in forms with inorganic cations and to quantitative determination of the water content in the membranes.

Electrochemical studies indicate that, due to the ion-exchange properties, some organic cations are selectively adsorbed on perfluorosulphonated polymers, and this can be utilized for their analytical determination, *e.g.* by cyclic voltammetry on modified electrodes⁴. Some compounds of this type are used *e.g.* as herbicides; therefore, from the environmentalist point of view it would be useful to develop a more general method for the determination of their trace amounts. Not all these compounds are, however, electrochemically active, and, therefore, we have selected IR spectroscopy as an alternative detection method; in this paper, a comparative study of some organic cations bound on Nafion film sulpho-groups is presented.

The thickness of the currently available Nafion membranes is unsuitable for measurement purposes because of low transparency in the IR range. Therefore, we attempted to prepare thin films by evaporation of polymer solutions. Only two procedures for solution preparation have been described in the literature. Martin *et al.*⁵ described the preparation of a 1% Nafion solution by dissolution in an autoclave in an ethanol-water mixture at 250° under vigorous stirring. The alcoholic

Nafion solution marketed by Aldrich Chemical Co. is probably prepared in this way. For the preparation of Nafion 117 solutions we tried to apply the Japanese patent⁶ describing Nafion 511 dissolution in hexamethylphosphoric triamide (HMPA) at temperatures 180–220°C. It appeared, however, that partial thermal degradation of the polymer may occur at this temperature, depending on the molar mass and internal structural arrangement of the polymer. This degradation is manifested *e.g.* by the yellowing of the solutions, and it is enhanced by the presence of water in HMPA. Polymers with carboxyl functional groups are particularly sensitive. Therefore we have sought an alternative solvent, permitting dissolution at a lower temperature. N,N-dimethylacetamide (DMAA) was found to be suitable; with it, partial dissolution of Nafion 901 (carboxyl functional groups) was attained already below 100°C.

Both with HMPA and DMAA, a part of the polymer remains in the form of insoluble aggregated particles; this is probably due to the circumstance that some fraction of the polymer with a low content of functional groups approaches by its properties the completely insoluble poly(1,1,2,2-tetrafluoroethylene). We have found that, under specific dissolution conditions, only a certain concentration can be reached due to the limited solubility of these particles. At longer standing of the solutions, *e.g.* in a refrigerator at temperatures near to 0°C, a partial reprecipitation of the polymer from the solution can occur. Assuming that the solubility of various macromolecules is given mainly by the ratio of the overall molar mass to the number of functional groups, it is evident that this procedure leads to a partial lowering of this ratio in the prepared films.

By evaporation of the polymer solutions, thin homogeneous layers were obtained which could be separated as films after saturation with water. For optimum transparency in the IR range, films 25 μm thick appeared as the most suitable, as they also exhibit sufficient mechanical strength. A comparison of the spectra of films prepared in this way with the spectrum of a film prepared by neutralization of the H^+ form by dimethylamine solution revealed that dissolution of the H^+ form of Nafion 117 in both HMPA and DMAA is connected with partial acid hydrolysis of the amide and the formation of the dimethylammonium form of the polymer. Therefore, the prepared films have first to be transformed back to the H^+ form by a solution of a suitable acid, *e.g.* 5M-HCl. In an aqueous solution of an amine or of tetraalkylammonium hydroxide, the H^+ form of the films is rapidly transformed to the corresponding ammonium form of the polymer, and the ion-exchange properties of the prepared films are thus preserved.

The films prepared from HMPA and DMAA yield identical IR spectra. In the range 1 300–400 cm^{-1} , bands typical of the poly(1,1,2,2-tetrafluoroethylene) skeleton⁷ were found, with wavenumbers (cm^{-1}) practically independent of the ionic form and the method of the film preparation: CF_2 sym. stretching 1 140–1 150 vs, br, CF_2 scissoring 633 s, CF_2 rocking 557 sh, 512 s, and the typical Nafion band¹ assigned to C—O—C sym. stretching 982 s, 969 sh. The very intense broad band with poorly pronounced maxima in the range 1 300–1 180 cm^{-1} originates from

the coincidence of CF_2 asym. stretching and SO_3^- asym. stretching. The SO_3^- sym stretching band appears at about $1\,055\text{ cm}^{-1}$ and its position depends somewhat on the type of the counter ion. The bands of ammonium cations in this range mostly overlap the polymer bands; on the other hand, the range $4\,000\text{--}1\,300\text{ cm}^{-1}$ is practically completely transparent, with the exception of the polymer bands at $2\,928$, $2\,857$, and $2\,368\text{ cm}^{-1}$ which, at the film thickness used, are of weak or very weak intensity, and of water bands which can be eliminated by drying. The band assignment of various ammonium cations is documented in Table I.

In the range of $\nu(\text{NH})$ the spectra of various types of ammonium cations are largely similar. The primary ammonium cations exhibit a broad, very strong band $\nu_{\text{asym}}(\text{NH}_3^+)$ with several shoulders, where the shoulder at $3\,105\text{ cm}^{-1}$ has been assigned to $\nu_{\text{sym}}(\text{NH}_3^+)$. Two bands in the spectra of secondary ammonium cations can be assigned similarly. The finding that even secondary ammonium cations exhibit two bands, could not so far be unequivocally explained; we assume that the splitting is caused by structural arrangement in the polymer film, similar as observed in the spectra of some halogenides⁸.

In contrast to the salts of halogen halide acids⁸⁻¹¹, the wavenumbers of all the measured cationic forms indicate very weak electrostatic anion-cation interaction, roughly comparable to the interaction in analogous tetraphenylborates^{12,13}. With the transition in the series from primary to tertiary ammonium cations, the strength of this interaction increases more rapidly than in the tetraphenylborates, *i.e.* similarly as with other oxygen-containing anions¹², *e.g.* ClO_4^- . Unexpectedly, the $\nu(\text{NH})$ wavenumbers are practically independent of the water content in the polymer; in all cases studied by us, the increase in the $\nu(\text{NH})$ wavenumber during the drying of a film originally saturated with water did not exceed 10 cm^{-1} . This is in agreement with the finding that the position of the residual water band in the films, about $3\,510\text{ cm}^{-1}/3\,570\text{ cm}^{-1}$ with R_4N^+ , indicates relatively weak hydrogen bonds¹⁴. On the other hand, there exist some indications that the $\nu(\text{NH})$ of some cations may depend somewhat on the method of the polymer film preparation, *i.e.* they may depend on structure and on the number of functional groups *per* mass unit.

The range of $\nu(\text{NH})$ partly overlaps the range of $\nu(\text{CH})$, and, consequently the bands of CH vibrations can only partly be assigned. The range of the CH bending modes, $1\,500\text{--}1\,300\text{ cm}^{-1}$ is characteristic. The bands of these vibrations are relatively sharp, they are typical of the various cationic forms and their wavenumbers are independent of film preparation or water content in the film. The wavenumber of the $\nu(\text{C}=\text{C})$ band is also independent of the experimental conditions.

It may be summarized that the described approach permits simple preparation of films which bind cations present in the studied solution by ion exchange on SO_3^- functional groups of the polymer. From electrochemical studies, the high exchange selectivity of some organic cations is known, leading to their considerable concentration in the polymer film. Using infrared spectroscopy, it is possible to identify the

TABLE I

Spectral properties of various ammonium cations in the form of sulphonium salts on 25 μm Nafion films prepared from an N,N-dimethyl-acetamide solution of the polymer. Deformation modes: A in case of $(\text{CH}_3)_n\text{NH}_3-n$ corresponds to asym. bending of (N^+-CH_3) methyl group, in other cases the band is formed by overlap of several deformation modes; B $\delta(\text{C}=\text{CH}_2)$; C sym. bending of methyl group (N^+-CH_3) or $\text{N}^+-\text{CH}_2\text{CH}_3$; D band overlap; E asym. bending; F sym. bending; G scissoring

Ionic form of polymer	Stretching (NH)		Stretching (CH_3)		$\delta(\text{NH})$	Deformation modes CH		
	$\nu(\text{C}=\text{C})$		asym.	sym.		A	B	C
NH_4^+	3 210 vs, 3 078 s	—	—	—	1 693 m, 1 440 vs	—	—	—
CH_3NH_3^+	3 176 vs, 3 105 sh	D	2 986 sh	—	1 625 m (E), 1 510 m (F)	1 472 m	—	1 434 w
$(\text{CH}_3)_2\text{NH}_2^+$	3 126 vs, 2 820 s	3 037 sh	2 978 w	—	1 613 m (G)	(1 476, 1 472) vs	—	1 423 w
$(\text{CH}_3)_3\text{NH}^+$	3 074 vs, 2 795 s	D	2 974 w	—	—	(1 487, 1 462) vs	—	1 423 w
$(\text{CH}_3)_4\text{N}^+$	—	—	3 046 m	2 971 w	—	1 494 vs	—	1 424 w
$\text{C}_2\text{H}_5\text{NH}_3^+$	3 167 vs, 3 105 sh	3 000 sh	D	—	1 626 m (E), 1 512 m (F)	1 480 m, 1 463 sh	—	1 405 m
$(\text{C}_2\text{H}_5)_2\text{NH}_2^+$	3 087 vs, 2 854 s	3 009 sh	D	—	1 621 m (G)	1 480 m, 1 463 sh	—	1 401 sh, 1 397 m
$(\text{C}_2\text{H}_5)_3\text{NH}^+$	3 054 vs, 2 822 s	3 000 sh	D	—	—	1 480 s, br	—	1 404 m, 1 398 sh
$(\text{C}_2\text{H}_5)_4\text{N}^+$	—	—	2 998 s	D	—	(1 490, 1 483) s (1 465, 1 448) s	—	1 400 s
$\text{CH}_2=\text{CHCH}_2\text{NH}_3^+$	3 154 vs, 3 105 sh	—	—	1 651 sh	1 623 m (E), 1 511 m (F)	1 462 m	1 432 s	—
$\text{CH}_2=\text{CHCH}_2\text{NH}_2^+$	3 076 vs, 2 852 s	3 010 sh	D	1 651 sh	1 615 m (G)	1 475 sh, (1 460, 1 456) s	1 435 sh	1 402 w
(C_2H_5)	3 062 vs, 2 791 s	D	2 978 sh	1 651 vw	—	1 483 s, 1 451 w	1 431 w	1 423 sh
$(\text{CH}_3)_2$	3 047 vs, 2 813 s	3 000 sh	D	1 651 vw	—	1 475 s, br	1 435 sh	1 402 m
$(\text{C}_2\text{H}_5)_2$	3 037 vs, 2 801 s	D	D	1 650 vw	—	(1 469, 1 462, 1 456) s	1 433 sh	1 402 w
$(\text{CH}_2=\text{CHCH}_2)_2$	—	—	—	—	—	—	—	—
NHC_2H_5^+	—	—	—	—	—	—	—	—

bound cations by means of vibrational bands in the range $4\,000-1\,300\text{ cm}^{-1}$. The method is not limited to a certain cation type: preliminary results indicate that it is suitable even for studies of reactions of cationic coordination compounds.

EXPERIMENTAL

Substance Used

Polymer membranes Nafion 117 in the H^+ form (E.I. DuPont de Nemours and Co., U.S.A.). Solvents hexamethylphosphoric triamide (Merck) and *N,N*-dimethylacetamide (Fluka), vacuum distilled prior to use. Amines: NH_3 , 26% aqueous solution, pure (Lachema); MeNH_2 (g), 97% (Merck); Me_2NH , 97% (Fluka); Me_3N , 30% aqueous solution (Merck); Me_4NOH , 10% aqueous solution, pure (Lachema); EtNH_2 , 99/100% (VEB Laborchemie Apolda); Et_3N , pure (Lachema); Et_4NOH , 10% aqueous solution, pure (Lachema); allylamine p.s. (Merck), freshly distilled; allylethylamine, diallylethylamine, allyldiethylamine, and allyldimethylamine were prepared as described in the literature^{15,16}, column distilled prior to use, and their purity was checked by GLC.

Preparation of Solutions and Polymer Films

Small cuttings of the membrane (300 mg) were dissolved for 12 h in 30 ml of *N,N*-dimethylacetamide under reflux (165°C) with stirring on a magnetic stirrer. After cooling, the undissolved polymer particles were removed by centrifugation. The concentration of the clear, colourless solution was determined gravimetrically after evaporation of a part of the solution and vacuum-drying of the residue (5 g l^{-1}). The preparation of the solution of Nafion 117 in hexamethylphosphoric triamide was described in our previous publication⁴.

Thin homogeneous polymer layers were prepared by evaporation of the solutions on a smooth glass plate under an infralamp. After saturation with water the layers were separated in the form of films which were transformed into the H^+ form by 5*M*-HCl, washed with distilled water and dried under an infralamp. Various ionic forms were prepared by soaking the films in the H^+ form for 1 h in 1–5% aqueous amine solution or in tetraalkylammonium hydroxide, washing with water and drying under an infralamp. Some ionic forms were also prepared by ion exchange of the Na^+ form with a solution of the hydrogenhalogenide of the respective amine; the identity of the form prepared in this way was verified by IR spectrum.

Infrared Spectroscopy

Films 8–35 μm thick were studied by the transmission technique in the range $4\,000-400\text{ cm}^{-1}$ on a Perkin-Elmer 684 spectrometer equipped with a PE 3600 data station. Very thin films ($<15\text{ }\mu\text{m}$) were placed between KBr discs for measurement. The mixture of indene (98.4%), camphor (0.8%) and cyclohexanone (0.8%) was used for wavenumber calibration.

REFERENCES

1. Falk M.: ACS Symp. Ser. 180, 139 (1982).
2. Ostrowska J., Narebska A.: Colloid Polym. Sci. 261, 93 (1983).
3. Hsu W. Y.: Macromolecules 16, 745 (1983).
4. Weber J., Janda P., Kavan L., Jegerov A.: J. Elektroanal. Chem. 199, 81 (1986).

5. Martin C. R., Rhodes T. A., Ferguson J. A.: *Anal. Chem.* *54*, 1639 (1982).
6. Toyo Soda Mfg. Co., Ltd., Sagami Chemical Research Center: *Jpn. Kokai Tokkyo Koho JP* *57*, 182, 345 (1982).
7. Moynihan R. E.: *J. Am. Chem. Soc.* *81*, 1045 (1959).
8. Chenon B., Sandorfy C.: *Can. J. Chem.* *36*, 1181 (1958).
9. Miller F. A., Wilkins C. H.: *Anal. Chem.* *24*, 1253 (1952).
10. Ebswroth E. A. V., Sheppard N.: *Spectrochim. Acta* *13*, 261 (1959).
11. Neville G. A., Regnier Z. R.: *Can. J. Chem.* *47*, 4229 (1969).
12. Werner G., Keller K.: *Chem. Ber.* *93*, 1982 (1960).
13. Nuttall R. H., Sharp D. W. A., Waddington T. C.: *J. Chem. Soc.* *1960*, 4965.
14. Sokolov N. D.: *Usp. Fiz. Nauk* *57*, 205 (1955).
15. Weston A. W., Ruddy A. W., Suter C. M.: *J. Am. Chem. Soc.* *65*, 674 (1943).
16. Cope A. C., Towle P. H.: *J. Am. Chem. Soc.* *71*, 3423 (1949).

Translated by D. Doskočilová.