



PROPERTY-STRUCTURE RELATIONSHIPS IN PARTIALLY SULPHONATED POLY(ETHYLENE TEREPHTHALATE)—1. INFRARED STUDIES

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Abstract—Lightly sulphonated poly(ethylene terephthalate)s containing 1.9 to 10.1 mol.% of $-\text{SO}_3\text{H}$ or $-\text{SO}_3\text{K}$ groups were studied with infrared spectroscopy. Characteristic absorption bands of sulphonic acid or potassium sulphonate groups attached to the aromatic nucleus of the copolyester chain were analysed in detail. It has been shown that in the studied copolyesters sulphonic acid groups are extensively associated through hydrogen bonds. The process of association is complex. Interaction of sulphonic acid groups with other proton acceptor and proton donor groups existing in the polymer chain superimposes the self-association of these groups. Associated structures such as dimers and greater aggregates of sulphonic acid groups and hydrogen bonded complexes composed of $-\text{SO}_3\text{H}$ groups and $-\text{C}(\text{O})\text{O}-$ and $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$ residues of polymer chain are mainly formed.

INTRODUCTION

A variety of effects arise from the incorporation of comonomers with functional pendant groups into polymer chains. In the case of carboxylic acids, sulphonic and phosphoric acids, alcohols, amines or amides, changes in physical properties of resulting copolymers are often identified with the hydrogen bonded structures formed [1–5]. Incorporation of sulphonic acid groups into both aliphatic and aromatic units of polymer backbone chains modifies the polarity of macromolecules, influences cohesive energy density and chain flexibility. Consequently, the properties of copolymers, in comparison with the parent polymers, are changed [6].

The purpose of the present work was to analyse in detail the association phenomenon through hydrogen bonds in sulphonated poly(ethylene terephthalate).

In the first part of this work, the results of IR studies in frequency region from 4000 to 400 cm^{-1} are presented. In the second part an influence of H-bonding on some physical properties of the studied copolyesters will be shown [7].

EXPERIMENTAL

Materials

The starting precursor polymer in this study, di-Me terephthalate-di-Me 2-potassium sulphoterephthalate-ethylene glycol copolymer (PETSTA/K), of the following chemical structure

was prepared in the Institute of Chemical Fibers (Łódź, Poland). Samples containing 1.9, 2.9, 4.4 and 10.1 mol.% of sulphoterephthalate comonomer units were used; they will be designated as PETSTA/K-X, where X = 2, 3, 5 and 10, respectively. Unmodified poly(ethylene terephthalate) (PET), used as the reference material was supplied by ZWCh 'Elana' (Toruń, Poland).

Prior to their use, the starting PETSTA/K and PET were purified by dissolution phenol-tetrachloroethylene (w/w = 1/1) and precipitated with methanol or ethanol. The sediment was filtered off, thoroughly washed with methanol (ethanol), dried in air and then kept in vacuum at 343 K for 100 hr. The powdered samples free from solvent were stored over P_2O_5 .

To characterize the chemical composition of the material, the mole fraction of potassium salt of sulphoterephthalic acid co-units and carboxyl-end groups have been determined quantitatively by the photometric titration method [8] and diethylene glycol links by the chromatographic method [9]. The characteristics of the samples are presented in Table 1.

The sulphonic acid derivative (PETSTA) was prepared from the starting copolyester (PETSTA/K) by ion exchange treatment over a strongly acidic macroporous type cation exchanger Amberlyst 15 (Rhom & Haas) in non-aqueous medium (m-cresol), as described elsewhere [8, 10]. After the ion exchange ($-\text{SO}_3^- \text{K}^+ \rightarrow -\text{SO}_3^- \text{H}^+$), polymer was precipitated from m-cresol solution with methanol or ethanol. The subsequent procedures such as washing and drying were as employed for PETSTA/K and PET.

Low-molecular model compounds: monopotassium salt of sulphoterephthalic acid and monopotassium salt of dihydroxyethylsulphoterephthalic acid were kindly provided by the Institute of Chemical Fibers (Łódź, Poland).

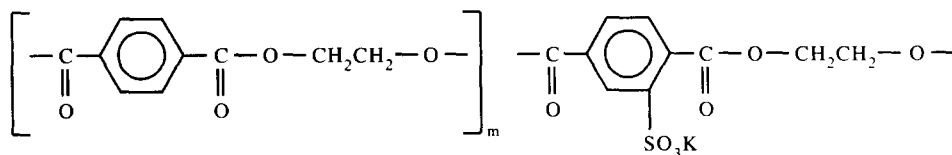


Table 1. Characterization data for PETSTA/K and PET

Polymer sample	Content of —SO ₃ K groups		Content of —COOH groups	
	mol. %	mol./kg × 10 ³	mol. %	mol./kg × 10 ³
PETSTA/K-2	1.9	96	2.5	40
PETSTA/K-3	2.9	148	3.1	46
PETSTA/K-5	4.4	219	4.1	49
PETSTA/K-10	10.1	478	7.4	56
PET			1.3	38

IR studies

PETSTA/K, PETSTA and PET samples were measured as thin films cast from trifluoroacetic acid solution and/or from trifluoroacetic acid and chloroform solution (*v/v* = 20/80). Solutions of the polymers in CF₃COOH (0.5–1.0 g polymer/10 cm³ solvent) were cast on polyethylene foils or directly on glass plates. Before casting, PE foil was stretched over a glass plate, cleaned with chloroform and soaked with CF₃COOH. Solutions of polymers in CF₃COOH/CH₃Cl mixture (1.0 g polymer/10 cm³ solvent) were cast on aluminium plates. After evaporation of the solvent in a stream of air, the films were scratched with a razor blade and dried in the vacuum oven at 50° for about a week. CF₃COOH content in polymer films was monitored by the IR method using the ν C=O band at 1790 cm⁻¹. All the samples were then stored in a desiccator over P₂O₅.

Low-molecular model compounds were analysed as Nujol mulls, KBr pellets and solutions in ethylene glycol.

The IR spectra were recorded using Perkin–Elmer Model 75, Carl Zeiss Specord M-80 and UR-10 spectrophotometers in the frequency region from 4000 to 400 cm⁻¹.

RESULTS AND DISCUSSION

1. Assignment of the IR absorption bands of sulphonated poly(ethylene terephthalate)

The assignment of the vibrational bands of sulphonated poly(ethylene terephthalate) has been based on: (a) comparison of the IR spectra of sulphonated polyester samples in different ionic forms containing H⁺ and K⁺ counterions, respectively, and non-sulphonated poly(ethylene terephthalate) (see Fig. 1); (b) spectral characteristics of the sulphonated and non-sulphonated compounds, both of low and high molecular weight, i.e.

- sulphoterephthalic acid and its monopotassium salt, as well as monopotassium salt of the di-hydroxyethyl-sulphoterephthalic acid, which can be treated as model compounds for the polymer units with sulphonic acid and metal sulphonate groups, respectively (see Fig. 2)
- sulphonated polymers, especially poly(styrene sulphonic acid) and its salts [11]
- poly(ethylene terephthalate) which corresponds to the main polymer backbone (see Fig. 1).

Vibrational spectra of poly(ethylene terephthalate), PET, have been studied in a number of papers and assignment of PET absorption bands has been reported in detail [12–15]. Thus, in our work we concentrated on the characteristic absorption bands of functional sulphonic acid and metal sulphonate groups attached to the aromatic nucleus of the polyester chain.

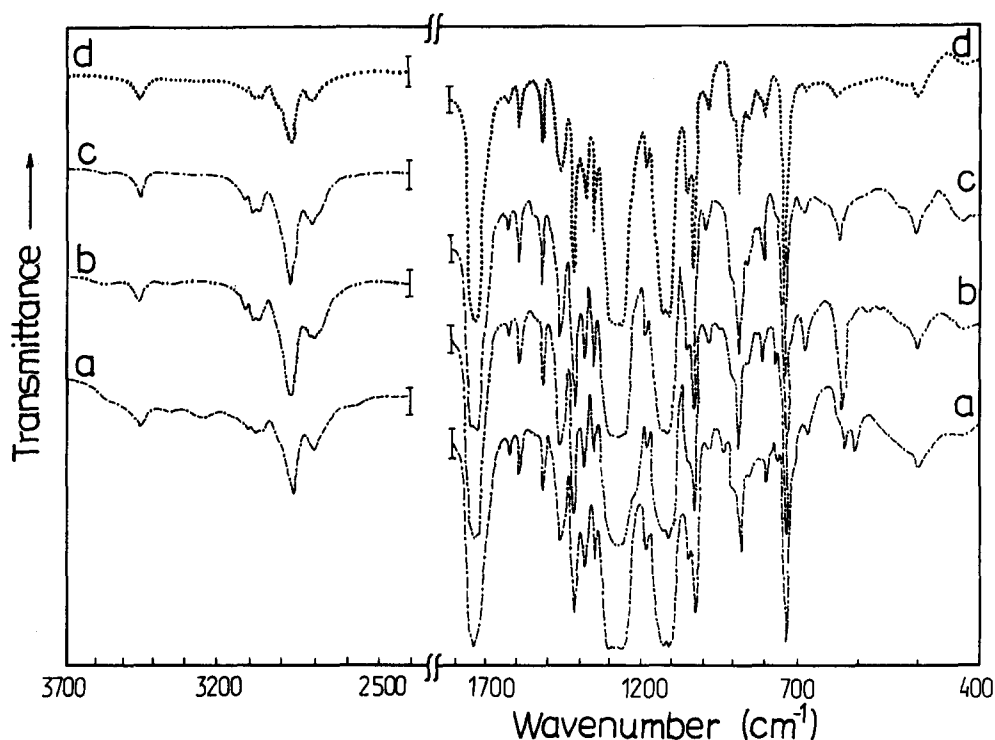


Fig. 1. Infrared spectra of sulphonated and non-sulphonated polymers: (a) PETSTA-10; (b) PETSTA/K-10; (c) PETSTA/K-2; (d) PET.

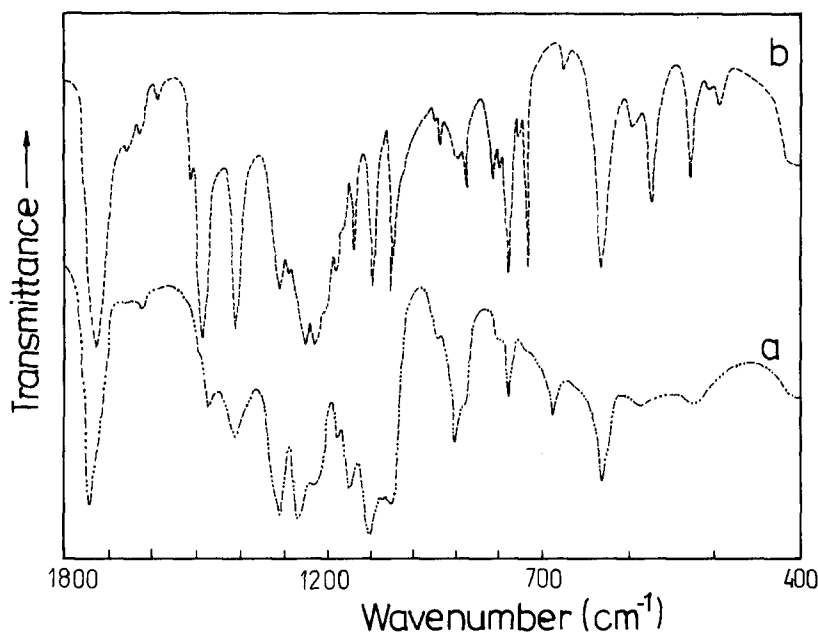


Fig. 2. Infrared spectra of low-molecular model compounds: (a) monopotassium salt of di-hydroxyethylsulphoterephthalic acid (diethylene glycol solution); (b) monopotassium salt of sulphoterephthalic acid (Nujol mull).

1.1. IR spectra of PETSTA/K

Infrared spectra of the potassium salt of poly(ethylene terephthalate-co-sulphoterephthalate), PETSTA/K, containing 1.9 and 10.1 mol.% co-units with $-\text{SO}_3\text{K}$ -groups and unmodified poly(ethylene terephthalate), PET, are presented in Fig. 1. As it is seen, only small differences between the spectra of PET and PETSTA/K polymers occur. It is caused by the poly(ethylene terephthalate) matrix being very rich in absorption bands. It masks most of the characteristic bands of $-\text{SO}_3\text{K}$ -groups. Thus the observation of S—O stretching vibrations is difficult, or even impossible, especially for lightly sulphonated samples.

In the spectra of PETSTA/K polymers only two bands related to $-\text{SO}_3\text{K}$ -groups may be observed. The first band occurs at 625 cm^{-1} . The second one is detected as a shoulder at about 1210 cm^{-1} . It is difficult to locate this shoulder exactly because of the high intensity of the near $\nu(\text{CO—O})$ vibration. The band at 625 cm^{-1} may be assigned to the C—S stretching vibration [11, 16]. Its intensity increases significantly with the content of the metal sulphonate groups. In the spectrum of the model compound—potassium sulphoterephthalate—this band is observed at 628 cm^{-1} .

Absorption bands corresponding to the symmetric and antisymmetric S—O stretching vibrations in SO_3^- ion of PETSTA/K should appear at about 1040 and 1200 cm^{-1} (doublet), respectively [11]. The $\nu_{\text{sym}}\text{SO}_3^-$ band is not found in the spectra of sulphonated PET. It is probably masked by the PET matrix band at 1042 cm^{-1} associated with the vibrations of ethylene glycol residue, $-\text{OCH}_2\text{CH}_2\text{O}-$, ($\nu_{\text{asym}}(\text{C—O})$, gauche).

The shoulder at about 1210 cm^{-1} , observed distinctly only for PETSTA/K-10 sample, is most

probably related to SO_3^- vibrations. It seems quite reasonable to assign it to the high energy part of the split antisymmetric vibration of SO_3^- ion. In the spectra of low molecular model compounds monopotassium salts of sulphoterephthalic acid and monopotassium salt of di-hydroxyethylsulphoterephthalic acid, $\nu_{\text{asym}}\text{SO}_3^-$ appears at 1030 cm^{-1} and $\nu_{\text{sym}}\text{SO}_3^-$ as doublet with the maxima at 1190 and 1208 cm^{-1} , respectively.

1.2. IR spectra of PETSTA

Figure 1 shows IR spectra of sulphonated poly(ethylene terephthalate) containing 10.1 mol.% of $-\text{SO}_3\text{H}$ and $-\text{SO}_3\text{K}$ groups, respectively. Some spectral changes can be observed after ion-exchange treatment of PETSTA/K. For PETSTA a new band at 935 cm^{-1} appears. It can be ascribed to the stretching vibration of the SO bond with the single-bond character in the $-\text{SO}_3\text{H}$ group, by analogy to the bands observed for another low- and high-molecular sulphonic acids [11, 17–20].

The change in the position of the complex band involving C—S stretching and ring vibrations for sulphonated PET after ion-exchange of counterions can also be observed. This band shifts from 625 cm^{-1} (acid) to 605 cm^{-1} (salt). A similar effect was observed earlier for poly(styrene sulphonic acid) [11] and poly(ethylene sulphonic acid) [20] membranes.

The bands corresponding to the symmetric and antisymmetric stretching vibrations of the SO bonds with double-bond character in the $-\text{SO}_3\text{H}$ groups are masked by the polyester matrix and therefore cannot be observed. In anhydrous sulphonic acids, both low- and high-molecular weight, the $\nu_{\text{sym}}\text{SO}_2$ and $\nu_{\text{asym}}\text{SO}_2$ stretching frequencies are reported in the regions of 1165 – 1150 and 1352 – 1342 cm^{-1} , respectively [17, 18].

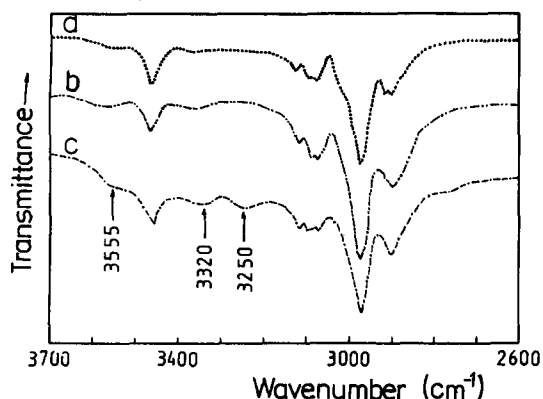
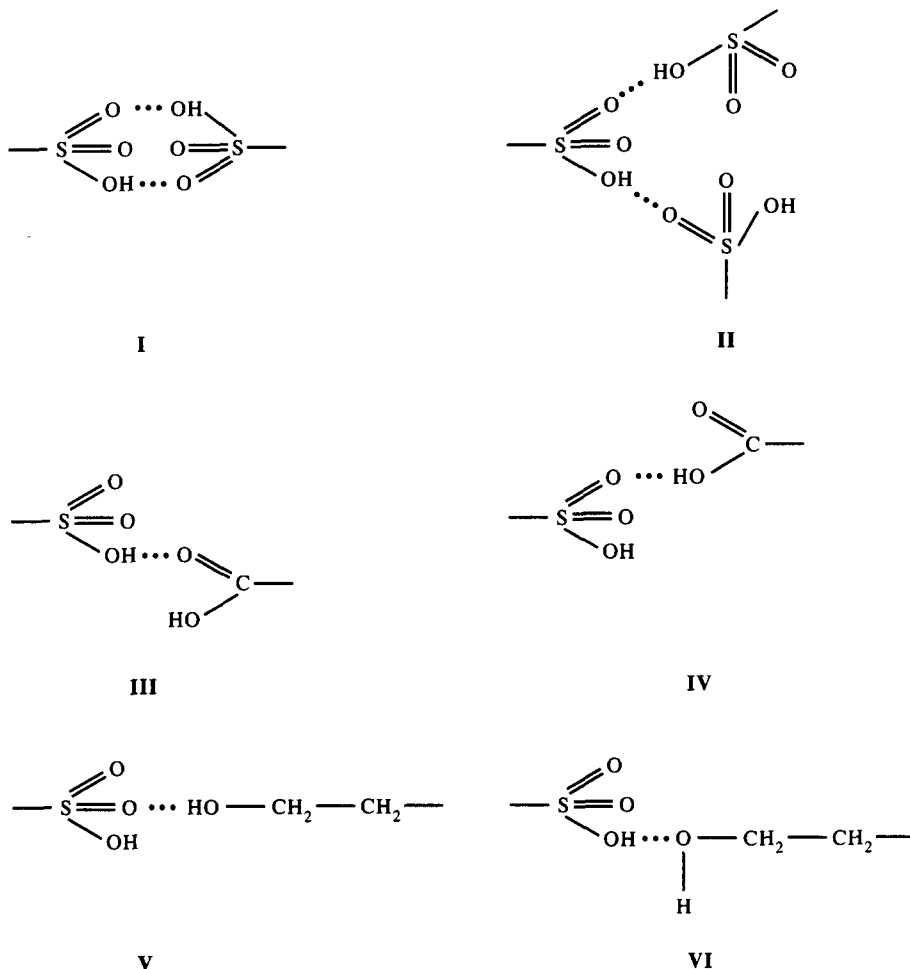


Fig. 3. Infrared spectra of sulphonated and non-sulphonated polymers in the νOH region: (a) PET; (b) PETSTA/K-10; (c) PETSTA/10.

Some differences between IR spectra of PETSTA and PETSTA/K in the $3600\text{--}3000\text{ cm}^{-1}$ frequency region are also detected (see Fig. 3). In the spectrum of PETSTA an additional band at 3250 cm^{-1} and the extensive broadening of the base line of C—H stretching frequencies at 2920 , 2970 and 3050 cm^{-1} occur. As we suppose, both the new band and the

base line broadening correspond to $\text{—SO}_3\text{H}$ groups involved in hydrogen bonds. Low-molecular as well as high-molecular sulphonic acids show generally two characteristic absorptions at about $3000\text{--}2900$ and 2400 cm^{-1} ascribed to the vibrations of the —OH groups in the hydrogen bridges mentioned above [17, 18]. The first band ($3000\text{--}2900\text{ cm}^{-1}$) is related to the O—H stretching vibration mode of sulphonic acid groups associated to cyclic dimers (Scheme 1, structure I) or greater associates [II], the second one (2400 cm^{-1}) corresponds to the first overtone of the O—H bending vibration mode of $\text{—SO}_3\text{H}$ groups engaged in a strong H-bond. For the simple alkane sulphonic acids and sulphonated chloropolyethylene, Nersasian and Johnson [21] have observed one band at 3030 cm^{-1} and the extensive broadening of the base line of the C—H stretching frequency, analogous to that observed in our studies of PETSTA. These two absorptions appear for p-toluene sulphonic acid in CCl_4 at 2955 and 2445 cm^{-1} , for polystyrene sulphonic acid at 2950 and 2405 cm^{-1} [11] and for perfluorosulphonic acid at 3000 and 2340 cm^{-1} [19], respectively. Thus, IR data for the sulphonated poly(ethylene terephthalate) indicate the association of sulphonic acid groups via hydrogen bonding.



Scheme 1 (structures I–VI) — continued opposite.

2. Hydrogen-bonded structures in PETSTA

In the studied polymer, various types both of proton donor [$-\text{OH}$ from $-\text{SO}_3\text{H}$ groups, $-\text{COOH}$ end-groups and $-\text{OH}$ end-groups] and proton acceptor groups [SO from $-\text{SO}_3\text{H}$ groups, $\text{C}=\text{O}$ from $-\text{C}(\text{O})\text{O}-$ ester groupings and $-\text{COOH}$ end-groups, an oxygen from diethylene glycol links and $-\text{OH}$ end-groups] are present. These groups are capable of forming different hydrogen-bonded structures, presented in Scheme 1, involving:

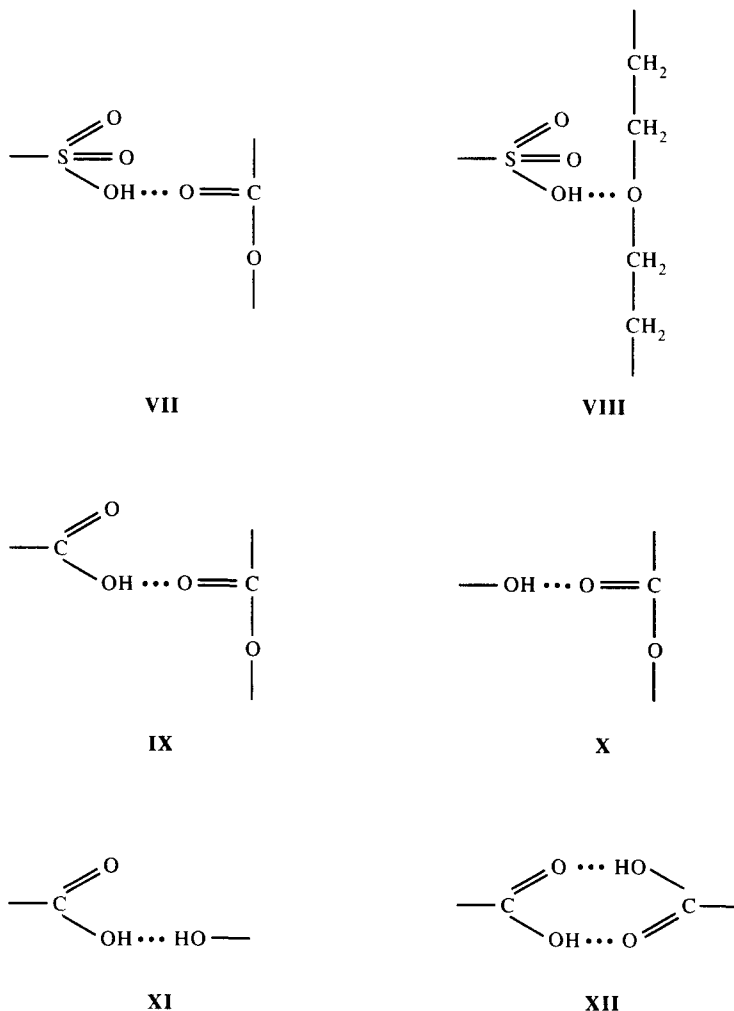
- (i) sulphonic acid groups [I, II]
- (ii) sulphonic acid groups and carboxyl [III, IV] or hydroxyl end-groups [V, VI]
- (iii) sulphonic acid groups and polar backbone chain fragments [VII, VIII]
- (iv) polymer end-groups and polymer chain fragments [IX–XII].

In general, the type, extent and distribution of hydrogen bonding in polymeric material is dependent on many factors, including the type and concentration of proton donor and proton acceptor groups, their relative proportions and the spatial arrangement

in the polymer chains. For the acid derivative of the studied copolyester sample PETSTA/K-10, the mean concentration of $-\text{SO}_3\text{H}$ groups in polymeric matrix is 10-fold higher than the concentration of end-groups [8, 9]. Thus, the formation of the H-bonded complexes of types III–VI involving sulphonic acid groups and end-groups seems to be less probable. For this polymer the self association of sulphonic acid groups and the association of these groups with $-\text{C}(\text{O})\text{O}-$ and $-\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2-$ residues of PET chains through H-bonds to structures I, II, VII and VIII seem to be the dominant processes.

We suppose that the band at about 3250 cm^{-1} visible in the IR spectrum of PETSTA presented in Fig. 3 is characteristic for the associated structures VII. This band can be ascribed to the $\text{O}-\text{H}$ stretching vibration mode of $-\text{SO}_3\text{H}$ groups engaged in H-bond formation with carbonyl of ester groups of PET backbone chain. This assignment is substantiated by the frequencies found for model systems containing sulphonic acid and ester groups [22].

The weak absorptions in the spectra of PETSTA, PETSTA/K and PET at about 3320 and 3555 cm^{-1} , which are observed only for thick film samples,



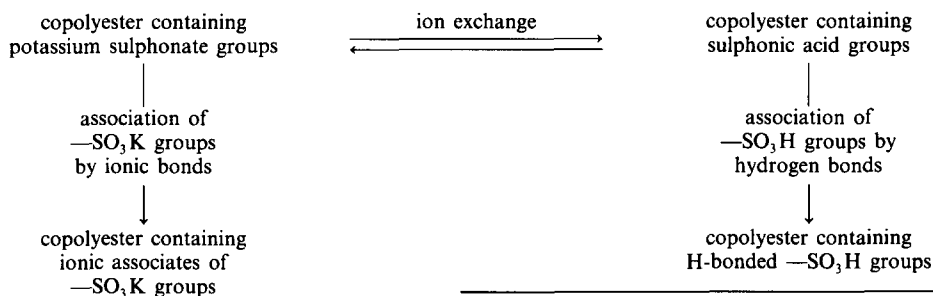
Scheme 1—continued (structures VII–XII).

correspond to the carboxyl and hydroxyl-end groups associated with ester residues of PET chain, analogous to those observed by Ward at 3290 and 3535 cm^{-1} for PET [23]. Langbein [24] has observed the same bands for aliphatic and aromatic polyesters at about 3300 cm^{-1} and 3555 cm^{-1} , respectively.

3. Behaviour of functional groups in PETSTA/K and PETSTA polymers

Sulphonated poly(ethylene terephthalate) has been studied earlier applying far-infrared spectroscopy [10, 22], SAXS and WAXS methods [22, 25] and differential scanning calorimetry [7, 22]. Far-infrared spectra of alkali metal salts of the sulphonated copolyester indicate the formation of ionic group associates of a multiplet or a low-order cluster type. DSC data [7] show that thermal characteristics (glass transition temperature, cold crystallization temperature, melting point and crystallinity) of PETSTA and PETSTA/K polymers are a consequence of H-bonding between sulphonic acid groups alone and/or sulphonic acid groups and polymer chain units and ionic interaction between potassium sulphonate groups, respectively.

In conclusion we can state that the behaviour of functional groups in lightly sulphonated poly(ethylene terephthalate) is directly connected to their ionic form and may be presented as follows:



CONCLUSIONS

The following conclusions can be drawn from spectral studies of the lightly sulphonated PET:

- (1) Sulphonic acid groups in this polymer are associated through hydrogen bonds.
- (2) Process of association of $-\text{SO}_3\text{H}$ groups is complex. H-bonded structures involving only sulphonic acid groups (dimers or greater associates) and sulphonic acid groups and $-\text{C}(\text{O})\text{O}-$ and $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$ groupings are predominant ones.
- (3) Hydrogen bonds act as weak crosslinks causing copolyester to assume a character of the three-dimensional networks and effect its properties [7].

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