

CHEMICAL TRANSFORMATIONS

OF POLYMERS. IX.*

AN INFRARED SPECTROSCOPY STUDY
OF STYRENE ANION EXCHANGER DEGRADATIONZ. VAŠÍČEK^a, J. KLABAN^a and J. ŠTAMBERG^b^a Research Institute of Synthetic Resins and Lacquers, Pardubice,^b Institute of Macromolecular Chemistry,
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The interpretation of infrared spectra has shown that besides the Hofman degradation also oxidative processes take place during the degradation of styrene anion exchangers by hydroxyl ions at presence of oxygen. The oxidation of the original exchange groups leads to the formation of carboxylic groups and in a smaller extent also tertiary alcoholic groups are formed on a polyvinyl chain.

In our previous paper¹ we used polymeranalogical transformations, paper and gas chromatography, as well as other methods of classical analytical chemistry to follow the degradation of crosslinked poly[(vinyl benzyl)trimethylammonium hydroxide] and its low molecular models (see also ref.²). In this communication we wish to report on infrared spectroscopy used as a tool for following the structural changes of an anion exchanger being degraded. To date infrared spectra of non-used anion exchangers³ have been published; there were attempts to characterize carboxylic groups in a degraded anion exchanger⁴. In this paper we shall describe the spectra of the original as well as degraded anion exchanger S-8-TM, by means of low molecular structure models. We also followed the change of particular absorption bands in the course of degradation.

EXPERIMENTAL

An S-8-TM anion exchanger, its low molecular weight models and their degradation were described in previous communication¹. The samples of the degraded anion-exchanger were transformed into the Cl-form, dried *in vacuo* over P₂O₅, ground in an electromagnetic vibrator at liquid nitrogen temperature⁵, and after the homogenization with KBr pressed into pellets. The KBr-pellet technique was also employed for taking spectra of some solid low-molecular weight

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compounds. Prior to measurement the pellets were dried for 12 hours over P_2O_5 at $50^\circ C/1$ Torr. The deuterated samples were obtained using the method due to Mass and Tolko⁶ by placing the pellets into a desiccator over heavy water for 16 hours at room temperature. Then the samples were dried by the above mentioned method. Liquid samples were measured in form of a 20 μ film between KBr discs, using Unicam SP 100 spectrometer with combination prism-grating. The measurements were performed in evacuated instrument calibrated before by indene mixtures and polystyrene.

RESULTS AND DISCUSSION

Infrared spectra of anion exchangers based on crosslinked poly-[(vinylbenzyl)trimethylammonium hydroxide], S-8-TM exchanger (*I*), and Amberlite IRA-400 (*II*), as well as their low molecular weight model, (isopropylbenzyl)trimethylammonium chloride (*III*), are almost identical (Table I, Fig. 1a, b). The differences are seen only in the region of $\tilde{\nu} \approx 3000$ cm^{-1} , where CH_2 - and CH_3 - groups absorb.

The decomposition of anion exchanger *I* by hydroxyl ions at elevated temperature and in the presence of oxygen causes complex changes in the spectrum (Fig. 1c); these are connected with formation of new groups. In order to characterize new absorption bands they were compared with the bands exhibited by low-molecular weight compounds* isolated as degradation products of substances modelling a structural anion exchanger unit¹ (Table II). The correctness of absorption band assignments was verified by measuring the intensity of the band in the course of exchanger degradation (Fig. 2). The results were then correlated with present hypothesis about degradative processes.

Absorption bands were characterized on the basis of Strásheim and Buijs's study³. Absorptions at 888 cm^{-1} , 974 cm^{-1} and 989 cm^{-1} whose intensity was decreasing during the degradation were attributed to the quaternary ammonium group. A 943 cm^{-1} band exhibited by degraded anion exchanger was assigned to an out-of-plane vibration of carboxylic OH group. Isopropylbenzyl alcohol, *IV*, and (isopropylbenzyl)-dimethylamine, *V*, absorb in the region of frequencies from 1015–1017 cm^{-1} . The corresponding band in the spectra of a degraded anion exchanger *I* is not changed by deuteration. Taking into account an increasing absorbance at $\tilde{\nu} \sim 1017$ cm^{-1} with degradation time it is concluded that this band corresponds to a C—O stretching vibration of alcohol. A 1089 cm^{-1} band of degraded anion exchanger which is also strongly exhibited by *IV* (1092 cm^{-1}) is thus ascribed to alcohol groups. Absorption band at 1139 cm^{-1} of a degraded anion exchanger *I* (whose intensity is lower by order of magnitude, compare Figs 1 and 2) was also seen in the spectrum of 7-hydroxycumencarboxylic acid (*VI*, $\tilde{\nu} = 1140$ cm^{-1}) and in the case of isopropylbenzoic acid (*VII*, $\tilde{\nu} = 1142$ cm^{-1}). With regard to the fact that, in the two former cases,

* The stereoisomers of *p*-chlorocumene obtained by chloromethylation of cumene (first preparation step) were not separated from one another in order to obtain a better model of polystyrene chloromethylation.

this band disappears upon deuteration, it is assigned to a deformation vibration of a hydroxyl group attached to a polyvinyl chain. Alcohol *IV*, amine *V*, acids *VI*, *VII* and acetylbenzoic acid (*VIII*) absorb, together with degraded anion exchanger, near 1186 cm^{-1} . This band is attributed to a C—N vibration of benzyltrimethylamino group on the basis of observation of its intensity–time dependence. Similar effect,

TABLE I

Positions of Absorption Bands ($\tilde{\nu}$ in cm^{-1}) and their Assignments for Cases of the Original Anion Exchanger S-8-TM (*I*), Anion Exchanger Amberlite IRA-400 (*II*) and (Isopropylbenzyl)trimethylammonium Chloride (*III*)

<i>I</i> ^a	<i>II</i>	<i>III</i>	Assignment ^b
703 s	702	708	CH deformation, out of plane (monosubstituted benzene)
—	—	731	
763 m	763	765	CH deformation, out of plane (monosubstituted and <i>o</i> -disubstituted and <i>o</i> -disubstituted benzene)
827 m	828	827	
855	857	855	
888 s	889	891	—N ⁺ (CH ₃) ₃
922 m	—	920	
974 m	977	976	—N ⁺ (CH ₃) ₃
989 w	—	994	—N ⁺ (CH ₃) ₃
1 019 w	—	1 020	
1 067 w	—	1 057	
1 219 w	—	1 220	
1 380 m	1 385	1 379	CH sym. deformation (—CH ₃)
1 415 m	1 417	1 408	C=C in plane (—CH ₂ C ₆ H ₃ RCH ₂)
1 422 m	1 427	1 419	CH deformation (—N ⁺ —CH ₂)
1 449 m	1 449	1 459	C=C in plane (C ₆ H ₅) + CH deformation (—CH ₂ — and CH ₃ —)
1 473	—	—	CH ₃ deformation asymmetrical in —N ⁺ (CH ₃) ₃
1 485 s	1 486	1 484	C=C in plane (C ₆ H ₅), CH ₃ in —N ⁺ (CH ₃) ₃
1 509 m	1 507	1 513	C=C in plane (C ₆ H ₅)
1 611 m	1 615	1 612	C=C in plane (C ₆ H ₅)
2 848	—	—	CH ₂ sym. stretch
—	—	2 868	CH ₃ sym. stretch (CH ₃)
2 918	2 915	2 924	CH ₂ asym. stretch (CH ₂)
—	—	2 956	CH ₃ asym. stretch
3 004	2 995	2 999	CH asym. stretch (—N ⁺ (CH ₃) ₃)
3 423	3 430	3 430	OH stretch (H ₂ O)

^a Relative absorption band intensity: w weak, m medium, s strong. Weak absorptions were observed at 1111, 1123, 1186, 1242, 1270 and 1313 cm^{-1} . ^b Assigned on the basis of Strasheim and Buijs's work³.

with regard to the behaviour of model compounds, is seen to occur round the frequency of 1270 cm^{-1} . The corresponding band of an anion exchanger does not change by deuteration and it is assigned, as well as the previous one, to a C—N vibration of amine groups. In the frequency region of $1360\text{--}1364\text{ cm}^{-1}$ there are also absorptions due to the alcohol *IV* ($\bar{\nu} = 1361\text{ cm}^{-1}$) and the amine *V* ($\bar{\nu} = 1362\text{ cm}^{-1}$) besides those exhibited by acids *VI*–*VIII*. The deuteration does not effect the anion exchanger absorption band ($\bar{\nu} = 1363\text{ cm}^{-1}$). It is possible that this band is due to a C—O valence vibration of an alcohol or to a symmetrical deformation vibration of CH_3 of a tertiary amine or due to a simultaneous effect of both groups because the absorption intensity increases with degradation time and appears in form of a shoulder on another band. A 1380 cm^{-1} band is attributed to a symmetrical deformation vibration of CH_3 group because the drop of its intensity with time corresponds to the disappearance of quaternary ammonium groups (compare with ref.³). Absorptions at 1473 cm^{-1} and 1485 cm^{-1} are assigned to a deformation asymmetrical vibration of methyl group in $-\overset{+}{\text{N}}(\text{CH}_3)_3$. The spectrum of tetramethylammonium chloride contains only a 1487 cm^{-1} band. It is possible, however, that

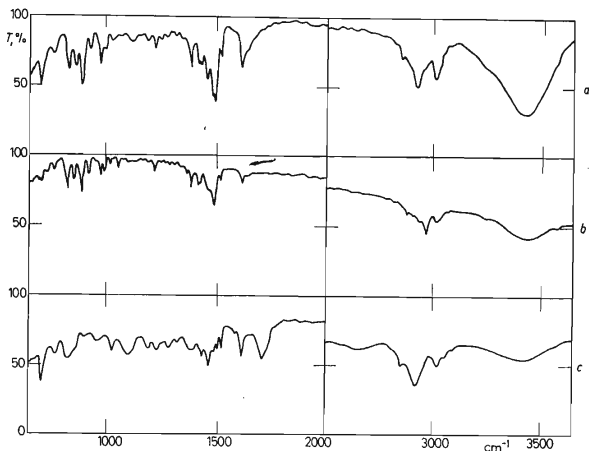


FIG. 1

Infrared Spectra

a Anion exchanger S-8-TM, *b* (isopropylbenzyl)trimethylammonium chloride, *c* anion exchanger S-8-TM degraded for 200 hours in 10N-KOH under an oxidative atmosphere.

the 1473 cm^{-1} band was formed by the split of the original band. The band in the frequency region of 1701 cm^{-1} in whose vicinity all the compared low molecular weight acids and the aldehyde *IX* absorb, corresponds to a $\text{C}=\text{O}$ valence vibration of carboxylic as well as aldehydic group. A 2668 cm^{-1} band exhibited by all low molecular weight acids changes during the degradation equally with the 943 cm^{-1} and 1701 cm^{-1} bands. This band is attributed to a valence vibration of carboxylic OH group. The absorption band at 3004^{-1} corresponds to an asymmetrical valence vibration of CH_3 groups in trimethylammonium group. The band at 3423 cm^{-1} is due to residual water in the sample and its intensity decreases with decreasing concentration of hydrophilic groups.

The time changes in the spectrum (Fig. 2) are in agreement with the results of the study of low molecular weight models degradation¹. The concentration of quaternary groups (888 cm^{-1} , 974 cm^{-1} , 989 cm^{-1} , 1380 cm^{-1} , 1473 cm^{-1} , 1485 cm^{-1} , 3004 cm^{-1}) decreases during degradation whereas the concentration of alcoholic groups (1017 cm^{-1} , 1089 cm^{-1} , 1363 cm^{-1}) increases; the amount of tertiary amine groups (1186 cm^{-1} , 1270 cm^{-1} or 1363 cm^{-1}) also increases after the initial induction period. The reason for non-zero values of relative extinction, that are not characteristic for the original anion exchanger *I* (bands at 1017 , 1186 , 1270 and 1363 cm^{-1}), is probably due to the choice of internal standard (Fig. 2) or the sensi-

TABLE II

Absorption Bands of Model Compounds ($\bar{\nu}$ in cm^{-1})

Isopropylbenzyl alcohol (*IV*), (isopropylbenzyl)dimethylamine (*V*), isopropylbenzoic acid (*VI*), 7-hydroxycumenecarboxylic acid (*VII*), acetylbenzoic acid (*VIII*), isopropylbenzaldehyde (*IX*). The meaning of the symbols w, m, s is the same as in Table I.

<i>IV</i>	<i>V</i>	<i>VI</i>	<i>VII</i>	<i>VIII</i>	<i>IX</i>
817 s	809 s	811 w, 820 w	820 m		828 m, 838 m
941 w	938 w	943 m	959 m	935 m	
1 015 s	1 017 s				
1 092 s	1 096 m				
		1 140 m	1 142 m		
1 179 m	1 171 m	1 182 m	1 188 m	1 183 m	
1 278 m	1 256 m	1 288 s	1 265 s	1 264 s	
1 361 s	1 362 s	1 360 w	1 364 m	1 360 m	1 363 w
1 379 s	1 379 w		1 376 m		1 385 m
1 416 m			1 416 m		
		1 426 s	1 424 m	1 424 m	1 425 w
		1 687 s	1 693 s	1 693 s	1 706 s
		2 673 m	2 670 m	2 665 m	

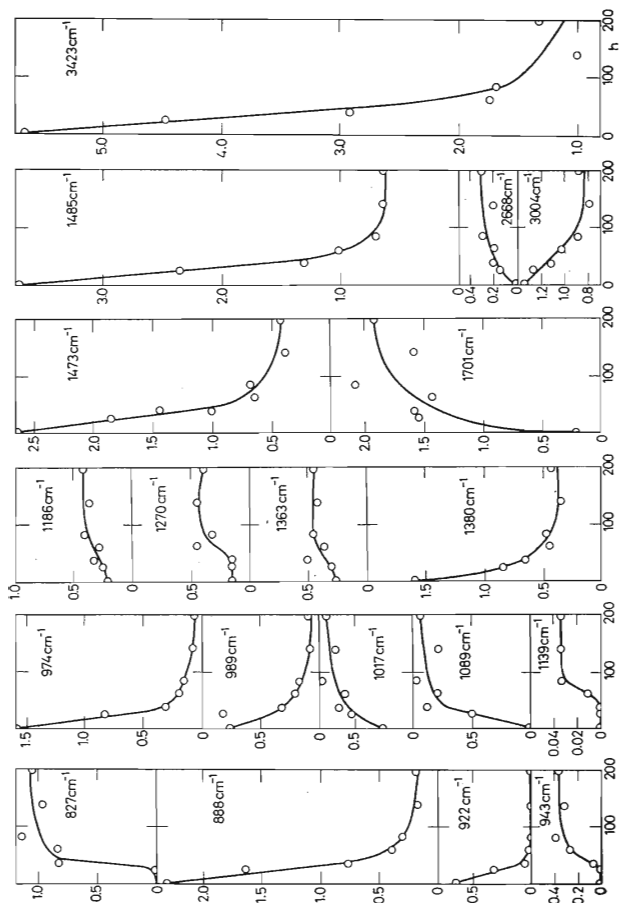


FIG. 2

The Time Dependence of Intensity of Certain Absorption Bands During the Degradation
Extinctions are expressed with regard to the 1509 cm^{-1} band used as an internal standard.

tivity of anion exchanger toward atmospheric oxidation. The carbonyl and carboxylic group content increases together with alcohols. The band at 1701 cm^{-1} may be due to aldehydic, ketonic or carboxylic group. The 943 cm^{-1} and 2668 cm^{-1} bands correspond to the hydroxyl attached to a carbonyl group. The change of a 1139 cm^{-1} band, attributed to the oxidation of tertiary carbons on the polyvinyl chain, takes place after a short induction period. The band intensity after completed degradation corresponds to c. 2-4% change of isopropylbenzoic acid VI to the acid VII.

The interpretation of infrared spectra of the degraded anion exchanger is in good agreement with the identification of degradation products of low molecular weight anion exchanger models. Hofman degradation of quaternary groups is a predominant reaction. Oxidation of the exchange group is only partial and the polyvinyl chain oxidation takes place only in a small extent.

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