Electrical conductivity of modified poly(vinyl chloride)

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MS received 7 December 1992; revised 3 May 1993

Abstract. Chemical modification of poly(vinyl chloride) (PVC) by dehydrochlorination with ethanolic KOH is found to yield modified PVC with conjugated polyene sequence. The semiconducting nature of ethoxide-modified PVC is illustrated with temperature dependence of conductivity (σ). The relative ratios (r) of conductivity, $\sigma_{\text{modified PVC}}/\sigma_{\text{unmodified PVC}}$, are greater than unity in the temperature range 50° to 180°C, r being maximum in the vicinity of glass-transition temperature (T_g). T_g inferred from conductivity–temperature profiles is found to be greater for modified PVC relative to unmodified PVC, which is explicable in terms of restricted free rotation limiting segmental motion. For comparison with the conductivity and T_g of ethoxide-modified PVC, LiCl-modified PVC and (aniline + $S_2O_8^{2-}$)-modified PVC have also been studied.

Keywords. Electrical conductivity; poly(vinyl chloride); modified poly(vinyl chloride); glass-transition temperature; conjugated polyene sequence; rubiconjugated polymer.

1. Introduction

Polyconjugated systems can be obtained from saturated macromolecules by thermal, radiation and chemical methods. Thermal treatment was one of the earliest methods applied to poly(vinyl chloride) (PVC) to get conjugated polymers of improved electrical conductivity (Takarzewski 1959; Slovokhotova and Astaf'ev 1961; Berlin *et al* 1962). However, thermal dehydrochlorination of PVC usually yields crosslinked polymers. Chemical modification by LiCl in dimethylformamide (Roth *et al* 1964) led to the formation of long conjugated polyenic sequences in PVC, the resulting polymers exhibiting strong light absorption near 550 nm and good semiconducting behaviour with electrical conductivity of the order of 10^{-11} to 10^{-10} S cm $^{-1}$ at room temperature. A recent patent (Ozawa *et al* 1986) on a highly semiconducting PVC film obtained by soaking a PVC film containing aniline in 0.1 N HCl containing $(NH_4)_2S_2O_8$ also encourages studies on modification of PVC to get semiconducting polymers. In the present study, chemical modification of PVC has been attempted to get semiconducting polymers of the rubiconjugated type. Evaluation of the glass-transition temperature of modified PVC from conductivity data is also an objective of the study.

The significance of ethanolic KOH in the dehydrohalogenation of alkyl halides led us to choose this reagent for modifying PVC by dehydrochlorination. In the case of PVC, once dehydrochlorination has started, the reaction can proceed in a zipper fashion since the liberated chloride anion can catalyse the β -elimination in the neighbouring position. This would lead to the creation of blocks of conjugated polyene sequences in PVC.

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Chart 1.

If such conjugated polyene sequences are actually produced in PVC, then the resulting polymer should have a higher electrical conductivity relative to the unmodified PVC. An electrical conductivity study of PVC and ethoxide-modified PVC would therefore reveal improvement in electrical conductivity due to the introduction of such conjugated polyene sequences in PVC. It is also of interest to evaluate the glass-transition temperature (T_g) of modified PVC from conductivity-temperature profiles since a higher T_g is expected for the modified polymer than for PVC due to the restriction on the free rotation and hence restricted segmental motion. Comparison with the already known chemical modification procedures for PVC warrants preparation of modified PVC by LiCl method and aniline + $\text{S}_2\text{O}_8^{2-}$ method and conductivity study of the modified samples. Hence the present study involves chemical modification by (i) ethoxide, (ii) LiCl and (iii) aniline + $\text{S}_2\text{O}_8^{2-}$, and semiconducting behaviour of the modified polymers relative to PVC along with T_g evaluation from conductivity data.

2. Experimental

A commercial sample of PVC (SriRam Vinyls, New Delhi, India) was employed. Intrinsic viscosity $[\eta]$, of the sample, determined from dilute-solution viscosity measurements using an Ubbelohde-type viscometer corresponds to 46.3 ml g^{-1} . The Mark-Houwink equation for PVC (Moore and Hutchinson 1963) in cyclohexanone at 25°C , $[\eta] = 2.08 \times 10^{-3} [\text{M}]^{0.56}$, where $[\eta]$ is given in dl g^{-1} , is used to find the molecular weight of PVC. The molecular weight of PVC thus evaluated corresponds to 9.5×10^5 . For such a high molecular weight polymer, conductivity and T_g are independent of molecular weight. Modification of PVC by ethoxide was accomplished by stirring well a suspension of 4 g of PVC in 50 ml of ethanolic KOH (a saturated solution of KOH in ethanol) at room temperature for about 48 h. Filtering, washing with water, and drying in vacuum afforded the light brown polymer. For modification by LiCl, 5 g of PVC, 3 g of LiCl and 50 ml of dimethylformamide (DMF) were mixed, stirred well for 24 h at room temperature, and poured into water, and the precipitated polymer was filtered and dried. A mixture of 5 g of PVC and 5 ml of aniline in about 100 ml of 0.1 N HCl was stirred for about an hour. After adding 2.5 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to the above reaction mixture, stirring was continued for about 24 h. The resulting modified polymer was filtered and dried.

For the modified PVC also, $[\eta]$ has been determined using cyclohexanone as the solvent at 25°C . For PVC-ethoxide, PVC-LiCl and PVC-(aniline + $\text{S}_2\text{O}_8^{2-}$), the $[\eta]$ values are 37.4, 75.0 and 71.0 ml g^{-1} respectively.

Electronic spectra were recorded in the visible region using a Carl-Zeiss UV VIS spectrophotometer. IR spectra were recorded with the sample in the form of KBr pellets in a Perkin-Elmer 983G IR spectrometer.

Electrical conductivity measurements were carried out using a Keithley electrometer model 614 for pressed polymer pellets in an evacuated cell (at $\sim 10^{-2}$ torr). Conductivity as a function of temperature is measured at least four times for each sample, in two heating cycles and in two cooling cycles. Generally conductivity data from the first heating cycle were higher, sometimes even two or three orders of magnitude higher, than those from the other three cycles. However, σ from the first cooling cycle, second heating cycle and second cooling cycle have been found to be consistent and reproducible. The conductivity data from the first heating cycle have therefore been discarded. A similar observation of high σ values for LiCl-modified PVC in the first heating cycle has also been made earlier (Roth *et al* 1964).

Seebeck coefficient measurements have been made as described in the literature (Hermann and Rembaum 1967).

3. Results and discussion

3.1 Electrical conductivity (σ) and T_g of unmodified PVC

PVC is an electrical insulator (Roff and Scott 1971) with $\sigma \simeq 10^{-14} \text{ S cm}^{-1}$. An even lower conductivity, $10^{-17} \text{ S cm}^{-1}$, has been reported elsewhere (Saito *et al* 1968). However, our present study on electrical conductivity of PVC (commercial sample prepared by suspension polymerization) gives a higher value of conductivity, of the order of $10^{-12} \text{ S cm}^{-1}$, at room temperature. Since thermal degradation of PVC with the elimination of HCl commences around 200°C , all the conductivity studies have been confined to $T < 200^\circ\text{C}$. Conductivity of unmodified PVC has been studied as a function of temperature in the temperature range 50°C to 180°C . The conductivity σ ranges from $6.74 \times 10^{-12} \text{ S cm}^{-1}$ to $2.39 \times 10^{-8} \text{ S cm}^{-1}$ in this temperature range (table 1). The negligible temperature dependence of conductivity in the low temperature range, 50° to 80°C , leads to an extrapolated value of conductivity at room temperature very nearly equal to $\sigma_{50^\circ\text{C}}$, i.e. $\sigma_{25^\circ\text{C}} \simeq \sigma_{50^\circ\text{C}}$. The temperature dependence of σ and also the magnitude of σ point to PVC being semiconducting. One of the reasons for this observed conductivity is probably *in situ* doping of PVC with ionic impurities during commercial preparation of PVC. Very slow thermal degradation of PVC at room temperature giving rise to HCl, the ionic impurity, would also be one of the factors contributing to the observed conductivity.

Conforming to the Arrhenius-type relation

$$\sigma = \sigma_0 \exp(-E_a/kT),$$

where σ_0 is a constant, E_a the activation energy of conduction, k the Boltzmann constant and T the absolute temperature, the semilogarithmic plot of $\log \sigma$ vs T^{-1} should be linear. However, the $\log \sigma$ vs T^{-1} plot for unmodified PVC (figure 1) is not a simple linear one but is made up of three intersecting straight lines. The Arrhenius-type equation (1) is obeyed but the different activation energies in the different temperature ranges for polymer systems demands separate Arrhenius-type relations with different activation energies, E_{a1} , E_{a2} , etc. for each temperature range. The effect of temperature is not only to cause an increase in generation and transport of charge carriers but also to cause changes in the polymer itself. For example, increase in temperature may change a glassy state of an amorphous polymer to the rubbery state. A temperature

Table 1. Electrical conductivity of PVC and modified PVC as a function of temperature.

$T(^{\circ}\text{C})$	$\sigma \times 10^{12}, \text{S cm}^{-1}$			$T(^{\circ}\text{C})$	PVC-aniline + $\text{S}_2\text{O}_8^{2-}$
	Unmodified PVC	PVC-ethoxide	PVC-LiCl		
50	6.74(6.92)	25.6	9.25	35	16900
55	6.61(6.51)	27.0	12.3	40	20500
60	6.48(6.00)	29.6	15.4	45	22600
65	6.36(5.88)	32.7	16.3	50	27300
70	5.96(6.00)	33.8	25.4	55	32200
75	5.75(5.45)	34.6	34.4	60	40300
80	6.74(6.20)	37.0	60.6	65	46100
85	6.91(6.91)	39.5	74.1	70	53700
90	13.1(11.95)	412	90.9	75	65600
95	19.9(19.9)	694	971	80	74200
100	43.3(43.0)	1050	1650	85	86700
105	83.3(83.9)	1500	3300	90	102000
110	136(136)	2070	5240	95	125000
115	297(285)	3040	10860	100	156000
120	581(620)	4780	16810	105	193000
125	1210(1220)	7810	26530	110	225000
130	1890(1890)	10500	39680	115	265000
135	2940(2940)	14900	55560	120	297000
140	4880(4890)	20200	84030	125	353000
145	6940(6950)	30500	112360	130	412000
150	9170(9210)	44800	151500	135	463000
155	12360(12300)	66700	217400	140	549000
160	15170(15200)	90900	270300	145	676000
165	17760(17800)	120500	322600	150	826000
170	20530(20500)	128200	400000		
175	22420(22200)	158700	476200		
180	23870(23400)	185200	625000		
185	—	217400	769200		
190	—	243900	1000000		

Values of σ in parentheses correspond to PVC with molecular weight 20,000 to 25,000

increase may also be accompanied by an order-disorder transformation or some other transition in the polymer. In other words, the effect of temperature in the case of semiconducting organic polymers is manifold relative to that in inorganic semiconductors. Since a change in conduction behaviour and activation energy of conduction would arise due to the above changes, a study of conductivity as a function of temperature would yield interesting information on these transitions in polymers. It is therefore not surprising that we get three intersecting straight lines in the semi-logarithmic plot (figure 1). If we denote the two critical temperatures as T_{c1} and T_{c2} and the activation energies in the different temperature ranges as E_{a1} for $T < T_{c1}$, E_{a2} for $T_{c1} < T < T_{c2}$, and E_{a3} for $T > T_{c2}$, it is noticed that the increase in conductivity with increasing temperature in the temperature range $T < T_{c1}$ is negligible, giving rise to the activation energy $E_{a1} \approx 0$. A sudden increase in conductivity is evident at T_{c1} . An increase in the slope of the $\log \sigma$ vs T^{-1} plot at $T > T_{c1}$, and hence $E_{a2} > E_{a1}$, is evident from the figure. The sudden increase in activation energy of conduction and conductivity at a critical temperature and hence conduction behaviour, in conjunction with the fact that the glass-transition temperature of the polymer is

Figure 1. Conductivity-temperature profile for unmodified poly(vinyl chloride) in the form of the semilogarithmic plot, showing T_{c1} and T_{c2} .

already known from a study of a basic property, makes it possible to correlate T_{c1} with T_g of the polymer as $T_{c1} = T_g$. The assumption made is that the activation energy of conduction in the rubbery state is greater than that in the glassy state of the amorphous polymer. This assumption is not unreasonable considering the flexibility of the macromolecule and the mobile chain segments in the glassy state. From the point of intersection of the two linear portions with change in slope in the plot of $\log \sigma$ vs T^{-1} , T_{c1} and hence T_g is inferred to be 84°C. This value agrees nicely with the literature value of T_g for PVC, 80°C to 85°C (Reding *et al* 1962; Bailey *et al* 1964; Barton *et al* 1971; Furukawa 1971; Liebman *et al* 1971; Usmanov *et al* 1971). The dielectric relaxation and conductivity studies of certain vinyl polymers including PVC (Saito *et al* 1968) showed that σ for PVC ranged from 10^{-17} to $10^{-12} \text{ S cm}^{-1}$ in the temperature range 25°C to 100°C and a break in the plot of $\log \sigma$ vs T^{-1} was correlated with glass-transition temperature. T_g from their data corresponds to 70°C, and this lower value may probably be due to the limited data in the conductivity-temperature profile.

Besides T_g , another transition at T_{c2} is also observed in our study (figure 1). A second change in the slope of the $\log \sigma$ vs T^{-1} plot, and hence change in activation energy, at 148°C indicates a transition above T_g for PVC. A transition at $T > T_g$ at 148°C may be attributed to the melting of the small fraction of crystallites due to syndiotactic form (Fuller 1940; Natta and Corradini 1956), which would generally

Table 2. Critical transition temperatures and activation energy of conduction in the various temperature ranges for PVC and modified PVC.

Polymer	T_{c1} (or T_g)(°C)	T_{c2} (°C)	E_{a1} (eV)	E_{a2} (eV)	E_{a3} (eV)
PVC (unmodified)	84	148	Negligible	1.484	0.595
PVC-ethoxide	87	162	0.123	1.046	0.595
PVC-LiCl	93	140	0.577	1.335	0.773
PVC-aniline + S ₂ O ₈ ²⁻	89	—	0.309	0.454	—

be present in PVC. The activation energy E_{a2} corresponds to 1.484 eV ($84^\circ\text{C} < T < 148^\circ\text{C}$), and it is to be noted that E_{a3} is generally less than E_{a2} but greater than E_{a1} (table 2).

Another PVC sample with molecular weight distribution 20,000 to 25,000 has been studied to find out the dependence of σ on the molecular weight of the polymer. The conductivity values are given in brackets in table 1 for this unmodified PVC. It is evident that there is negligible difference in the conductivities of the two unmodified PVC samples, showing that σ is independent of molecular weight for a high molecular weight polymer. Furthermore, a plot of $\log \sigma$ vs T^{-1} also shows the same two phase transitions at the same temperatures, showing that the phase transition temperatures are also independent of molecular weight of PVC.

3.2 Conjugated polyene sequence in ethoxide-modified PVC

Ethoxide-modified PVC absorbs in the visible region (figure 2) whereas unmodified PVC does not. Creation of isolated double bonds in PVC due to dehydrochlorination cannot lead to such long wavelength absorption as observed in the case of ethoxide-modified PVC. Since blocks of conjugated polyene sequences are produced in PVC, the modified polymers can, in fact, be regarded as acetylene–vinyl chloride block copolymers. The conjugated blocks produced in PVC are expected to have the absorption characteristics of simple conjugated polyenes. For example, the absorption bands for PVC modified by ethoxide can be correlated with those of a simple conjugated polyene, despite the solvent shift, as follows. The absorption spectrum of ethoxide-modified PVC (figure 2) exhibits four intense maxima, bands A to D, besides the hump at 357 nm. The four intense bands at 370, 392, 418 and 439 nm for the modified PVC closely parallel the ones observed for eicosadecaene (Sondheimer *et al* 1961), namely 370, 391, 413 and 446 nm, and the hump at 358 nm. The close resemblance between the absorption characteristics of ethoxide-modified PVC and eicosadecaene, a simple conjugated polyene with ten double bonds, suggests that the conjugated polyene block in modified PVC is a decaene unit. The extinction coefficients ($\text{ml g}^{-1} \text{cm}^{-1}$) as a function of λ are also presented (table 3).

The IR spectrum of ethoxide-modified PVC shows, besides all other characteristic bands for PVC (Luther *et al* 1959), the C=C stretching vibration of a conjugated system (Conley 1972) in the wavenumber range $1590\text{--}1640 \text{ cm}^{-1}$ (figure 3), supporting the inference based on the visible absorption spectrum that conjugated polyene units are present in modified PVC.

Figure 2. Visible absorption spectra of ethoxide-modified poly(vinyl chloride). Solvent: cyclohexanone. Absorbance as a function of concentration of PVC.

Table 3. Extinction coefficients as a function of λ for modified PVC.

PVC-ethoxide		PVC-LiCl		PVC-aniline + $\text{S}_2\text{O}_8^{2-}$	
λ (nm)	ϵ ($\text{ml g}^{-1} \text{cm}^{-1}$)	λ (nm)	ϵ ($\text{ml g}^{-1} \text{cm}^{-1}$)	λ (nm)	ϵ ($\text{ml g}^{-1} \text{cm}^{-1}$)
357	102	347	221	350	2760
370	97	365	230	357	3100
385	93	389	235	362	3480
392	93	412	229	370	3510
410	80	436	229	375	3540
418	71	456	218	385	3140
439	62	475	200	396	2670
458	56	490	188	408	2110
484	42	515	153	446	1080

3.3 Electrical conductivity and T_g of ethoxide-modified PVC

The electrical conductivity data as a function of temperature for ethoxide-modified PVC (table 1) show that the conductivity ranges from 2.56×10^{-11} to $2.44 \times 10^{-7} \text{ S cm}^{-1}$ in the temperature range 50° to 190°C . The conductivity increases very slowly with increasing temperature, from 50° to 85°C , the activation energy of conduction E_{a1} being 0.123 eV in this temperature range. A sudden jump in conductivity is evident (figure 4) when the temperature increases from 85° to 90°C . On the basis of our earlier arguments, it is discernible that this critical transition temperature lying between 85°C and 90°C is the glass-transition temperature. T_g is thus found to be

Figure 3. Infrared spectra of modified poly(vinyl chloride) in KBr pellet.

Figure 4. $\log \sigma$ as a function of T^{-1} for ethoxide-modified poly(vinyl chloride). Sudden jump in conductivity at T_g (87°C) indicated by dotted line.

87°C for ethoxide-modified PVC and the sudden increase in conductivity at T_g , indicated by the dashed line in figure 4, is explicable in terms of increase in free volume at T_g . At $T > T_g$, the temperature dependence of conductivity is greater (table 2), as evident from the slope of the $\log \sigma$ vs T^{-1} plot. A decrease in slope at the

Figure 5. $d \ln \sigma / dT$ vs T plot for ethoxide-modified poly(vinyl chloride) exhibiting maximum at T_g (87.5°C).

second critical transition temperature of 162°C occurs (figure 4), giving rise to an activation energy of conduction $E_{a3} = 0.595 \text{ eV}$ (table 2).

Relative to unmodified PVC, ethoxide-modified PVC shows a higher conductivity and this is evident nicely from the relative ratio of σ , $r = \sigma_{\text{modified PVC}} / \sigma_{\text{unmodified PVC}}$. The ratio varies from 4 to 6 only in the temperature range 50° to 85°C whereas there is a sudden increase in the vicinity of T_g , r being 32 at 90°C and 35 at 95°C .

In addition to the plot of $\log \sigma$ vs T^{-1} , a plot of $d \ln \sigma / dT$ vs T can also be used to evaluate T_g in the case of ethoxide-modified PVC. Since there is a sudden jump in conductivity in the vicinity of T_g , the increment in conductivity, $d\sigma$, for a certain increase in temperature, dT , is found to be quite high in the glass-transition temperature range. A maximum in the plot of $d \ln \sigma / dT$ vs T at $T = T_g$ is therefore expected. This, in fact, is realized, as is evident from figure 5. T_g from the $d \ln \sigma / dT$ vs T plot is found to be 87.5°C , which is in good accord with the value of 87°C inferred from the $\log \sigma$ vs T^{-1} plot.

T_g for ethoxide-modified PVC is higher than T_g of unmodified PVC. This is explicable on the basis of the structural differences in the two polymers. Ethoxide-modified PVC, which can be regarded as a vinyl chloride-acetylene block copolymer as mentioned earlier, has conjugated polyene blocks with restricted free rotation due

to the presence of double bonds. This would limit the segmental motion in ethoxide-modified PVC and hence the higher T_g is understandable. Since the conjugated blocks introduced are small, the increase in T_g is also small.

3.4 Comparison with other modified PVCs

LiCl-modified and (aniline + $S_2O_8^{2-}$)-modified PVCs, which also exhibit visible absorption (figures 6 and 7) and possess conjugated polyene sequence (IR spectra in figure 3) were studied and compared with ethoxide-modified PVC. Conductivity-temperature profiles are presented for the two systems in the form of semilogarithmic plots of $\log \sigma$ vs T^{-1} (figures 8 and 9). Even though the conductivity of LiCl-modified PVC is lower than that of ethoxide-modified PVC in the low temperature range (50° to 90°C), a reverse trend is noticed in the high temperature range, $\sigma_{\text{PVC-LiCl}} > \sigma_{\text{PVC-ethoxide}}$ (table 1). T_g of LiCl-modified PVC is found to be 93°C from conductivity data, and a second critical transition temperature is also observed, $T_{c2} = 140^\circ\text{C}$. The higher value of T_g for LiCl-modified sample relative to ethoxide-modified sample can be interpreted in terms of the long conjugated polyene sequence in the former as evident from the λ_{max} value from the data of extinction coefficients as a function of λ (table 3), λ_{max} for PVC-LiCl $> \lambda_{\text{max}}$ for PVC-ethoxide.

PVC modified by aniline + $S_2O_8^{2-}$ exhibits maximum conductivity (table 1) of all the three modified PVCs. Even at 35°C , the conductivity is found to be $1.69 \times 10^{-8} \text{ S cm}^{-1}$. The room temperature value of σ , $\sigma_{25^\circ\text{C}}$, corresponds to $1.1 \times 10^{-8} \text{ S cm}^{-1}$. The temperature dependence of conductivity is quite low compared to other modified samples of PVC, $\sigma_{150^\circ\text{C}}$ being only $82.6 \times 10^{-8} \text{ S cm}^{-1}$ (table 1). The increase in slope at $T > T_g$ is not as distinct as in the case of PVC-LiCl and PVC-ethoxide. However it is possible to infer the T_g of the polymer to be 89°C (figure 9). The activation

Figure 6. Visible absorption spectra of LiCl-modified poly(vinyl chloride). Solvent: cyclohexanone. Absorbance as a function of concentration of PVC.

Figure 7. Visible absorption spectra of poly(vinyl chloride) modified by aniline + $S_2O_8^{2-}$ at different concentrations of the polymer.

Figure 8. Conductivity-temperature profile in the form of $\log \sigma$ vs T^{-1} for LiCl-modified poly(vinyl chloride).

Figure 9. Conductivity-temperature profile in the form of $\log \sigma$ vs T^{-1} for poly(vinyl chloride) modified by aniline + $S_2O_8^{2-}$.

Figure 10. $d \ln \sigma / dT$ vs T plot for LiCl-modified poly(vinyl chloride) exhibiting maximum at T_g (92.5°).

energy of conduction E_{a2} at $T > T_g$ is much less relative to E_{a2} of the other two modified samples (table 2).

The plot of $d \ln \sigma / dT$ vs T is also utilized in the case of PVC-LiCl to infer the T_g from the maximum in the plot (figure 10). T_g inferred thus, 92.5°C, shows very good agreement with T_g (93°C) from the $\log \sigma$ vs T^{-1} plot.

Despite the fact that PVC film modified by aniline + $S_2O_8^{2-}$ gave rise to a highly semiconducting film (Ozawa *et al* 1986) with σ of the order of $10^{-2} \text{ S cm}^{-1}$, the same reagents used for powdered PVC yielded modified PVC with σ only of the order of $10^{-8} \text{ S cm}^{-1}$ in the present work. The difference in conductivity would be due to different extents of conjugation in the modified sample, which in turn stems from the difference in the concentrations of the reagents and other experimental conditions used in the preparation of modified PVC.

Relative to LiCl-modified PVC prepared earlier (Roth *et al* 1964), LiCl-modified PVC prepared by us exhibits a lower conductivity, by nearly an order of magnitude. This is attributed once again to the longer polyenic sequences in the former compared to the latter. Roth *et al* (1964) observed only one critical transition temperature which ranges from 80°C to 104°C for the modified PVC with different percentages of conjugated double bonds. This is probably due to limiting the conductivity study up to $\sim 150^\circ\text{C}$. The relative magnitudes of E_{a2} and E_{a1} , $E_{a2} > E_{a1}$, observed by them also confirm the validity of the assumption made in the evaluation of T_g in the present work, E_a in the rubbery state of the polymer is $> E_a$ in the glassy state of the polymer. A higher activation energy for the rubbery state of the polymer relative to the glassy state has also been observed in the case of elastomeric ionenes (Somoano *et al* 1970).

Ethoxide-modified PVC as well as the other two samples of modified PVC prepared and studied for comparison with the former belong to the class of rubiconjugated polymers with limited conjugation. Hence the improvement in conductivity is also subject to limitation. The advantageous properties of PVC coupled with this semi-conducting nature may however prove to be fruitful.

3.5 Seebeck coefficients of modified PVC

Measurements of Seebeck coefficients for the modified PVCs show that they exhibit very large and negative Seebeck coefficients (Q) of the order of mV K^{-1} . For example, Q is found to be -2.17 mV K^{-1} at 324 K for ethoxide-modified PVC, -1.79 mV K^{-1} at 316 K for PVC-LiCl and -1.96 mV K^{-1} at 319 K for (aniline + $S_2O_8^{2-}$)-modified PVC, which are closely related. The data suggest that electrons are the majority carriers for the transport process and the modified PVCs are n -type semiconductors. PVC modified by LiCl shows a transition from n -type to p -type semiconductivity at high temperatures, $\sim 425 \text{ K}$.

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