Eur. Polym. J. Vol. 24, No. 8, pp. 803–806, 1988
Printed in Great Britain. All rights reserved

0014-3057/88 $3.00 + 0.00

IONIC INTERACTIONS IN SULPHONATED POLY(ETHYLENE TEREPHTHALATE)—II. THERMAL STUDIES

BARBARA OSTROWSKA-GUMKOWSKA and JADWIGA OSTROWSKA-CZUBENKO
Nicholas Copernicus University, Institute of Chemistry, ul. Gagarina 7, 87-100 Toruń, Poland

(*Received* 27 *April* 1987; *in revised form* 15 *June* 1987)

Abstract—The glass transition temperatures of alkali metal salts of sulphonated poly(ethylene terephthalate) were found for the range of sulphonation from 1.9 to 10.1 mol%. It was found that T_g depends largely on the degree of sulphonation rather than on the detailed properties of the cation. The results suggest that some change in the state of ion aggregation occurs above a sulphonation level of roughly 5 mol%, in agreement with previous findings obtained by the f.i.r. method.

INTRODUCTION

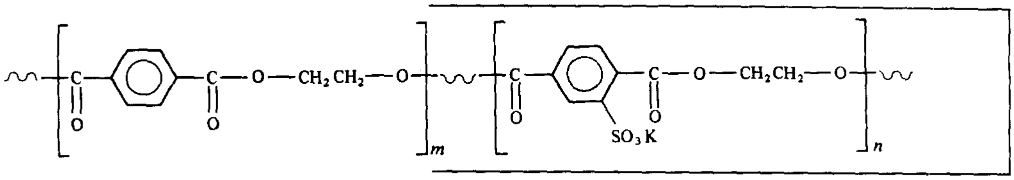
Ion–ion and ion–polymer dipole interactions in ionomers alter the supermolecular structure of these materials as compared to their non-ionic counterparts and consequently affect the glass transition temperature, mechanical properties, the melt rheology and other physical properties. It has been shown that the glass transition temperature (T_g) of an ionomer is considerably higher than that of a polymer matrix before the introduction of ions. This increase in T_g depends on the nature of the cation, the effect being greater as the ionic forces increase. According to Eisenberg [1], T_g of an ionomer is the temperature at which ion pairs forming ionic cross-links dissociate and hence there is a temperature at which the thermal energy approaches the electrostatic binding energy of an ion pair. Datye and Taylor [2] suggest that an ionic cluster as a whole acts as a cross-link and the glass transition of an ionomer corresponds to the onset of orientational disorder or "melting" in a cluster of ionic dipoles.

We now report on the glass transition temperatures of alkali metal salts of sulphonated poly(ethylene terephthalate) (PETSTA/Me). The studied copolyester is an ionomer with relatively high backbone chain stiffness. As shown by the f.i.r. method [3], sulphonate groups in this copolyester aggregate to multiplets or low-order clusters. In this work we examine ionic heterogeneities in PETSTA/Me from differential scanning calorimetry studies.

EXPERIMENTAL

Materials

The random copolymer, poly(ethylene terephthalate-co-potassium salt of sulphoterephthalate), PETSTA/K, of the following chemical structure: containing from 1.9 to 10.1 mol% of SO_3K-groups was used. Samples of the polymer were kindly supplied by the Institute of Chemical Fibres (Łódź, Poland). The characteristics of the samples are presented in Table 1. Lithium, sodium and caesium salts (PETSTA/Me) of the copolymer and its sulphonic acid derivative (PETSTA) were prepared from a starting sample containing 10.1 mol% SO_3K-groups by means of ion-exchange treatment. The ion-exchange was performed over a strongly acidic macroporous type cation exchanger Amberlyst 15 (Rhom & Haas) in a non-aqueous (*m*-cresol) medium as described previously [4]. The ion-exchanged polymer samples were precipitated from solution with dry methanol (or ethanol) and dried under vacuum at 343 K for 72 hr. Then the samples were stored in a desiccator over P_2O_5 for at least 10 days before loading into DSC-cells. The degree of replacement of K^+-ions by X^+-ions ($X^+ = Na^+, Li^+, Cs^+, H^+$) in the resulting polymeric salts was determined through potassium analysis using flame photometry. The ion-exchange was found to be essentially complete. Because the sample preparation was performed in a non-aqueous medium, very little or no bulk water was present in the polymeric salts. It could be assumed therefore that after additional drying, the samples were free of water.



DSC-measurements

Values of T_g of the copolyester samples were found with a Perkin–Elmer DSC-1B calorimeter, previously calibrated with standards of known melting points. As T_g deduced by the calorimetric analysis depends on the thermal history of a sample and on the speed of heating or cooling, the DSC-measurements were performed in the following sequence. First, a DSC-scan of each dry sample (14 mg) was recorded during heating (20 K/min) from ambient temperature (298 K) up to a temperature 30 K above the melting point. The sample was then held at that temperature for 10 min, quenched by rapid cooling (nominally 320 K/min) to 298 K and rescanned at 4 K/min. The same measurements were performed at rates of heating of 8, 16, and 32 K/min. An O_2-free atmosphere was used in all the measurements.

The value of T_g was taken from the measured DSC-curves applying the midpoint method. To make T_gs comparable for various samples, the transition data obtained at four scan rates were extrapolated to zero rate. It was established through the duplicate experiments that reading and baseline errors lead to experimental error in T_g of ±2–3 K.

Table 1. Characterization data for PETSTA/K copolyester

Sample	Content of SO_3K-groups (mol%)	Content of SO_3K-groups (mol/kg × 10^3)	Content of DEG links (mol%)	Content of COOH-groups (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

RESULTS AND DISCUSSION

Influence of sulphonation level on T_g

The DSC-results for the copolymer PETSTA/K containing from 1.9 to 10.1 mol% co-units with SO_3K-groups are presented in Fig. 1a. They have been obtained at a rate of heating $\beta = 8$ K/min. As can be seen, the glass transitions for the samples are distinct and depend on the sulphonation level. As the degree of sulphonation reaches 10.1 mol%, the glass transition becomes broader. To demonstrate the influence of the heating rate on T_g of the studied samples, Fig. 1b shows the DSC-scans recorded for PETSTA/K-10 at $\beta = 4$, 8, 16 and 32 K/min, re-

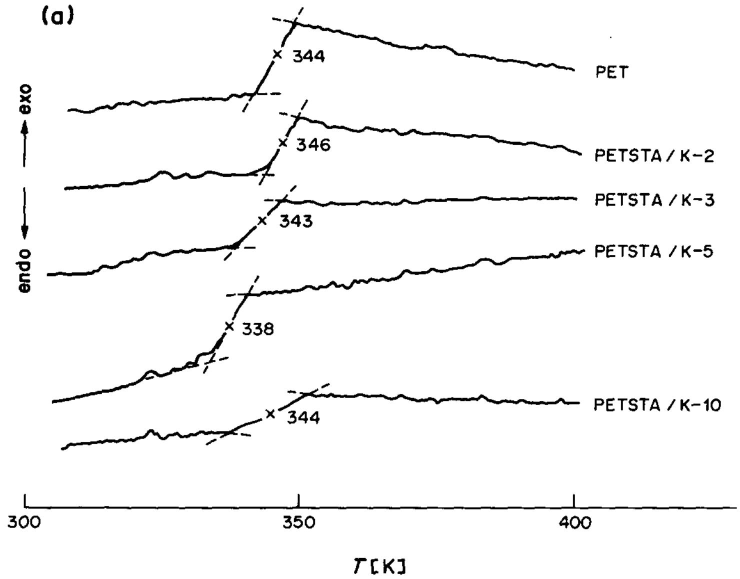


Fig. 1a. DSC results for PETSTA/K and PET ($\beta = 8$ K/min).

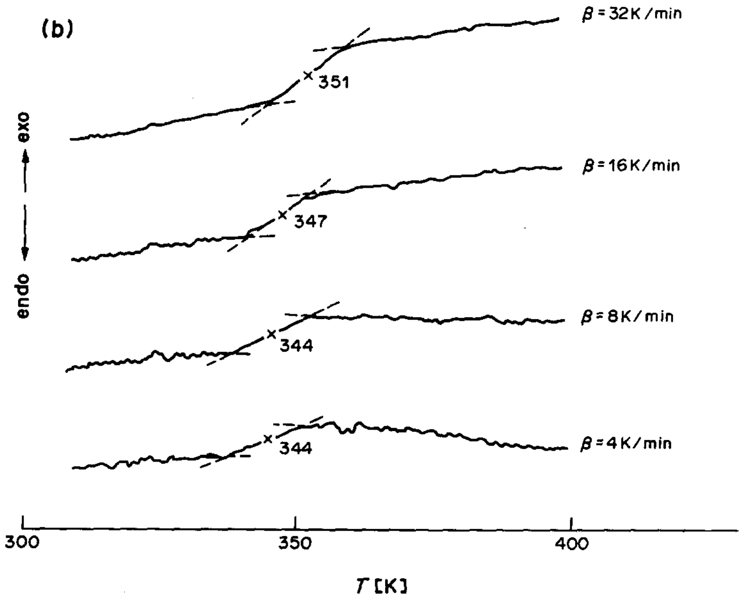


Fig. 1b. DSC curves at different heating rates for PETSTA/K-10.

Table 2. Glass transition data for PETSTA/K, PET and PDET

Sample	Glass transition temperature, T_g^0 (K)	Temperature[a] range of the glass transition (K)	Glass transition[b] temperature of non-ionic matrix, T_g^0 (K)
PETSTA/K-2	344	5	337
PETSTA/K-3	340	8	336
PETSTA/K-5	337	7	334
PETSTA/K-10	343	15	331
PET	340		
PDET	289		

[a] β = 8 K/min. [b] Calculated by means of the Fox equation.

spectively. It is evident that the onset of departure from the baseline and the inflection point of the baseline shift are displaced upwards in temperature as the heating rate is increased. This dependence is presumably the result of a lag in the transfer of heat to the sample and a lag in heat transfer within the sample [5]. As we have shown, the graph of log T_g vs β is linear for all the studied samples. The temperature obtained on extrapolating the line log $T_g = f(\beta)$ to zero rate (T_g^0) is assumed to be the correct transition temperature. Table 2 summarizes the extrapolated T_gs together with the data for the unmodified poly(ethylene terephthalate) (PET). Column 3 shows the temperature range of the glass transition.

The variation of T_g with the content of ionic co-units seems to be unusual as compared with that observed for classical ionomers. According to the results of Eisenberg and other authors [6–10], T_g of an ionomer increases linearly with the concentration of salt groups, or eventually begins to deviate substantially from the typical copolymer-type behaviour by rising sharply. It has been suggested that the difference from the copolymer behaviour correlates with the critical concentration of salt groups necessary for the formation of microphase-separated domains.

To explain the T_g vs SO_3K-content dependence observed in our studies, the presence of a relatively high content of diethylene glycol (DEG) links in the backbone of our copolyester must be considered. The formation of DEG units is the main side reaction during the synthesis of PET and the modified PET [11–15]. DEG links are more flexible than glycol links and cause T_g of poly(ethylene terephthalate-co-diethylene terephthalate) to decrease somewhat as the mole fraction of DEG in the copolyester chain increases [16] attaining 289 K for pure poly(diethylene terephthalate) (PDET) [17].

A lack of knowledge of T_g for the fully sulphonated PET, i.e. for the polymer containing one sulphonate group for each repeat unit and T_g for fully sulphonated PDET does not permit us to verify whether or not the observed variation in T_g^0 (Table 2) obeys a simple random copolymer equation. Moreover, the sequence distribution of four kinds of co-units present in the copolyester and its influence on T_g of the studied tetracopolymer are unknown.

To solve the problem, partially at least, we have calculated T_g^0 for a non-ionic polymer matrix consisting of ethylene terephthalate and diethylene terephthalate units containing DEG links in amounts as in the studied ionic materials. In our calculations, the Fox equation [18] was used according to the suggestion of Campa *et al.* [17]. The results are given in Table 2. Figure 2 presents the numerical values of $\Delta T_g^0 = (T_{g\,\text{ionic copolymer}}^0 - T_{g\,\text{matrix}}^0)$ as a function of the sulphonation level. We suppose that ΔT_g^0 may be regarded as a measure of increase in stiffness of the ionic copolyester backbone due to the incorporation of bulk sulphonate groups on polymer chains and, on the other hand, to the possible intermolecular and intramolecular interactions of the groups. As can be seen, ΔT_g^0 diminishes slightly as the sulphonation level increases to 4.4 mol% and then it increases significantly for the sample PETSTA/K-10. These results suggest that, at the lower levels of sulphonation (up to 5 mol%), the influence of the flexible DEG links on the overall stiffness of copolyester chains prevails over the stiffening effect of sulphonated co-units. The distinct increase in ΔT_g^0 observed at a sulphonation level of 10.1 mol% suggests that in the sample PETSTA/K-10 the stiffening effect caused by intermolecular interactions of SO_3K-groups forming physical crosslinks of some kind predominates over the composition effects. This statement is in agreement with our earlier results obtained by the f.i.r. method [3] which suggest the aggregation of metal sulphonate groups in the studied ionic copolyester.

Influence of the cation nature on T_g

In evaluating T_g of the studied copolymer PETSTA/Me as a function of cation field strength, we have prepared our starting copolyester sample PETSTA/K-10 in the form of lithium, sodium and caesium salts. In Fig. 3 the obtained values of T_g^0 for the salts are plotted against q_c/a, where q_c is the charge of the cation, a is the distance between centres

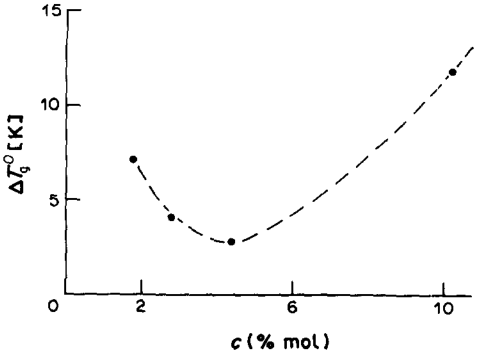


Fig. 2. Dependence of ΔT_g^0 on the sulphonation level for PETSTA/K.

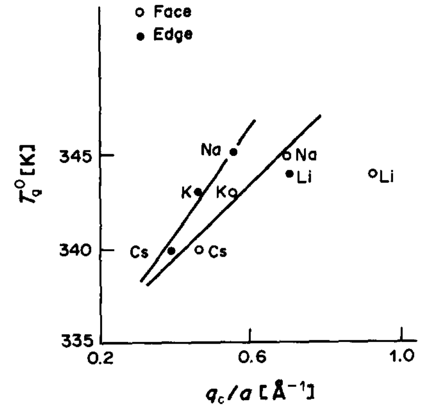
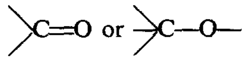


Fig. 3. Dependence of T_g^0 on q_c/a for PETSTA/Me-10; Me = Li, Na, K, Cs.

of the charge. The numerical values of q_c/a have been calculated for the tetrahedral structure of the sulphonate anion [19]. This introduces the possibility of a bond length of 0.82 Å if the cation co-ordinates to the edge of the anion, and another bond length (0.47 Å) if the cation co-ordinates to the face. The results suggest that T_g for PETSTA/Me slightly depends on the nature of the cation at the sulphonation level of 10.1 mol%, although the data for sodium, potassium and caesium salts seem to fit a single curve when T_g^0 is plotted vs q_c/a. The data corresponding to a lithium salt deviate from linearity in the dependence between T_g^0 and q_c/a, in agreement with our previous findings from the f.i.r. method. As we have shown [3], the forces between lithium cations and anionic sulphonate groups incorporated into a PET-matrix are covalent in nature, as in the case of the lithium salt of poly(styrene sulphonic acid) ionomers [20]. The results indicate additionally (Fig. 4) that T_g^0 varies slightly as the cation–sulphonate site force constant (k) increases. The values of k have been calculated assuming the tendency of alkali metal cations for six-co-ordination, i.e. to octahedral surrounding by oxygen atoms [19].

For the acid derivative of the studied copolyester sample PETSTA/K-10, the glass transition has not been detected, probably because of the presence of highly organized rigid hydrogen-bonded structures involving sulphonic acid groups or sulphonic acid groups and



residues of PET-chains. These structures were detected by i.r. spectroscopy [21].

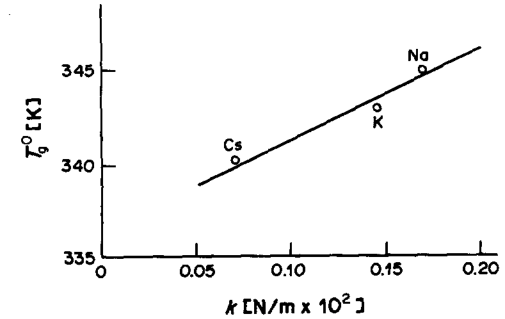


Fig. 4. Dependence of T_g^0 on k for PETSTA/K-10; Me = Na, K, Cs.

CONCLUSIONS

The following conclusions may be drawn from the studies of T_g of the ionic copolyester PETSTA/Me as a function of ion concentration and type of the cation.

(1) The broadened region of glass transition and the distinct increase in ΔT_g^0 observed at an ion content of 10.1 mol% may be interpreted as evidence that some change in the state of ion aggregation has occurred above the sulphonation level of roughly 5 mol%.

(2) The presence of a single T_g for the copolyester shows that only a small fraction of ionic groups forms high-order aggregates.

(3) T_g varies very slightly with the nature of the cation. All of them presumably found their lowest available free-energy structures to be ionic aggregates.

Acknowledgement—This work was supported by the Polish Academy of Science within the Project MR-I-31.

REFERENCES

1. A. Eisenberg and M. King. *Ion-Containing Polymers: Physical Properties and Structure* (Edited by R. S. Stein). Academic Press, New York (1977).
2. K. Datye and P. L. Taylor. *Macromolecules* **17**, 1414 (1984).
3. J. Ostrowska-Czubenko and B. Ostrowska-Gumkowska. *Eur. Polym. J.* **24**, 65 (1988).
4. J. Ostrowska, B. Ostrowska-Gumkowska, D. Rybińska and G. Szymański. *Acta Polym.* **36**, 691 (1985).
5. S. Strella and P. F. Erhardt. *J. appl. Polym. Sci.* **13**, 1373 (1969).
6. A. Eisenberg. *Contemp. Top. Polym. Sci.*, Vol. 3 (Edited by Michel Shen), p. 231. Plenum Press, New York (1979).
7. A. Eisenberg and M. Navratil. *Macromolecules* **6**, 604 (1973).
8. H. Matsuura and A. Eisenberg. *J. Polym. Sci., Polym. Phys. Edn* **14**, 1201 (1976).
9. D. Rahrig and W. J. MacKnight. In *Ions in Polymers Adv. Chem. Ser.*, Vol. 187 (Edited by A. Eisenberg) p. 77. American Chemical Society, Washington D.C. (1980).
10. A. Noshay and L. M. Rebeson. *J. appl. Polym. Sci.* **20**, 1885 (1976).
11. H. Renwen, Y. Feng, H. Tinzheng and G. Shiming. *Angew. Makromolek. Chem.* **119**, 159 (1983).
12. W. Mössner and B. Vollmert. *Makromolek. Chem., Rapid Commun.* **6**, 527 (1985).
13. S. Fakirov, I. Seganov and E. Kurdova. *Makromolek. Chem.* **182**, 185 (1981).
14. H. Krzystek. *Chem. Vlakna* **27**, 194 (1977).
15. P. Fischer, H. Drechsler, H. J. Flath, W. Berger and F. Billig. *Faserforsch. TextTech.* **27**, 418 (1978).
16. J. Guzman and J. G. Fatou. *Eur. Polym. J.* **14**, 943 (1978).
17. J. G. Campa, J. Guzman, J. Abajo and E. Riande. *Makromolek. Chem.* **182**, 3163 (1981).
18. T. G. Fox. *Bull. Am. Phys. Soc.* **1**, 123 (1956).
19. J. A. Lefelar and R. A. Weiss. *Macromolecules* **17**, 1145 (1984).
20. V. D. Mattera Jr and W. M. Risen Jr. *J. Polym. Sci., Polym. Phys. Edn* **22**, 67 (1984).
21. J. Ostrowska-Czubenko. Prepared for publication.