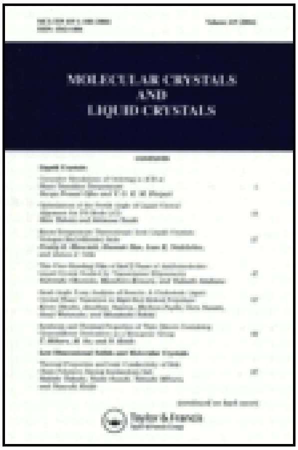


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Glass Transition Effects in Polyelectrolyte Glasses with Linear and Non-Linear Optical Properties

Janusz Pecherz [a], Marian Kryszewski [a], Gerhard Wegner [b] & Wolfgang H. Meyer [b]

[a] Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-362, Łódž, Poland

[b] Max-Planck-Institut für Polymerforschung, Postfach 3148, W-6500, Mainz, Germany

To cite this article: Janusz Pecherz , Marian Kryszewski , Gerhard Wegner & Wolfgang H. Meyer (1992): Glass Transition Effects in Polyelectrolyte Glasses with Linear and Non-Linear Optical Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 216:1, 79-84

To link to this article: http://dx.doi.org/10.1080/10587259208028753

Mol. Cryst. Liq. Cryst. 1992, Vol. 216, pp. 79–84
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

GLASS TRANSITION EFFECTS IN POLYELECTROLYTE GLASSES WITH LINEAR AND NON-LINEAR OPTICAL PROPERTIES

JANUSZ PECHERZ, MARIAN KRYSZEWSKI
Center of Molecular and Macromolecular Studies,
Polish Academy of Sciences, 90-362 Łódż, Poland

GERHARD WEGNER AND WOLFGANG H.MEYER
Max-Planck-Institut für Polymerforschung,
Postfach 3148, W-6500 Mainz, Germany

Abstract Linear and non-linear optical properties of polyelectrolyte glasses can be modified by proper choice of the organic dye counterions. The glass transition temperatures of these polyelectrolyte glasses with organic dyes as counterions were measured by DSC. A correlation with concentrations and chemical structures of anionic dyes was clearly shown. It was also found that glass transition temperatures of polyelectrolyte glasses are lower in the presence of solvent traces.

INTRODUCTION

Thermal behaviour of ionenes depends on the length of the alkylene spacer between the ionic sites and the type of counterion. For the crystalline ionenes the melting temperature shows a dependence on the type of counterion and decreases for a given concentration with the increasing length of the alkyl chain between the ammonium groups. The decomposition temperature seems to depend to some extent on the nucleophilicity of the counterion[1].

The fact that aliphatic ionenes with tosylate, triflate and tetrafluoroborate do not recrystalize after quenching from the melt allowed glass transition temperature of these polymers (Tg) to be determined by DSC[2].

The ionenes with divalent counterions, e.g. ($ZnBr_4^{2-}$) do not recrystalize when cast from solution, while the ionenes with tosylate, triflate and tetrafluoroborate as counterions undergo recrystallization after a long time. The Tg values of these ionenes are strongly affected by thermal history of the sample[2].

Recently it was demonstrated that the glasses can be made from polyelectrolytes (PEL) with glass forming properties being adjusted by the chemical structure of the ionic polymer and the optical properties being tuned by the choice of the appropriate counterions[2].

Recently it was also shown for the first time that polyelectrolyte glasses based on polycations with anionic dyes as counterions can be prepared. Third harmonic generation and antenna effects have been found in PEL glasses. The optical quality of these glasses was excellent since the dye is homogeneously dispersed and bound by coulombic interactions[3].

In the following we want to report briefly on the preparation and the glass transition temperature of PEL with anionic dyes as counterions.

EXPERIMENTAL

Dye containing PEL were obtained by ion-exchange starting from polymers : I-10-Me-Br , I-6,10_{stat}-Me-Br, I-6-Me-Br , I-Do,Pip-Me-Br and S-6,10_{stat}-Me-CH_3OSO_2 prepared as bromide and methylsulphate with anionic dyes: EO, MeY, Crl, APX and CrMMO by the same procedure as described previously [3,4].

The exchange of counterions was also carried out by the following method: polycation bromide 10^{-3}mole was dissolved in 50 ml DMF (DMSO) and equimolar DMF (DMSO) solution of sodium salt of dyes was added. The resulting soluble polycation-X salt was isolated by precipitation in water and was filtered off.

The polymer dye salt is soluble in polar solvents like DMF, NMF and was cast from this solvent to provide optically clear films. The actual concentration of the dye was determined by elemental analysis , UV-VIS spectra of the solid glassy films or by ^{1}H NMR after redissolving the films. The results are shown in Table I. Thermal properties were measured using DuPont 910 differential scanning calorimeter with a heating rate of 10 K/min.

RESULTS AND DISCUSSION

Table I shows the glass transition temperatures of the polycations under study. It was found that for the same polycation the Tg value increases linearly with the molar content of the dye-counterion (e.g. for I-10-Me-EO and I-6-Me-Crl in Fig.1a. However for the polycation S-6,10$_{stat}$-Me-Crl a nonlinear dependence of Tg on dye concentration was observed (Fig.1b). This fact can be elucidated by non-symetrical and statistical distribution of positive charges in the polymer chain. For the same polycation and similar molar concentration of dye Tg is higher for the dyes of greater volume.

Similarly as for polycations with inorganic counterions[4], the increase of Tg for PEL can be correlated with the decrease of the distance between charged N^+ or S^+ in the polycation chain i.e with the charge density on polymer chain e.g. I-10-Me-Crl, S-6,10$_{stat}$-Me-Crl and

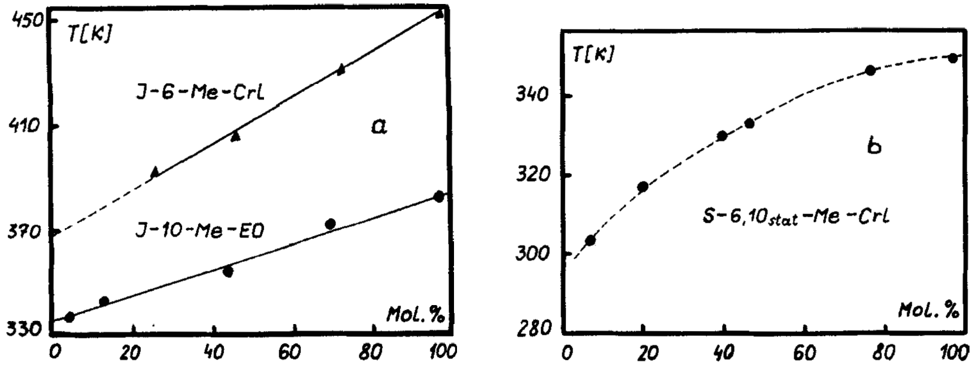
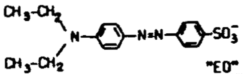
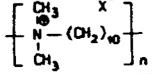
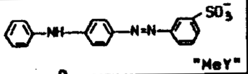
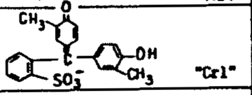
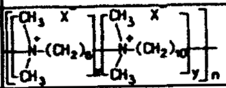
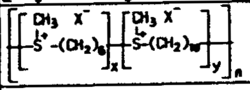
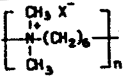
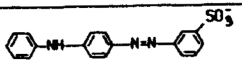
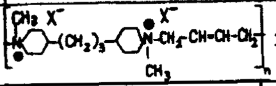
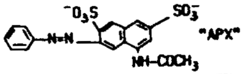
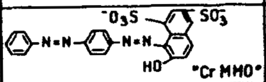


Fig.1 Dependence of Tg on dye concentration in I-6-Me-Crl I-10-Me-EO (a) and in S-6,10$_{stat}$-Me-Crl (b).

TABLE I Structures and glass transition temperatures investigated of the polycations

	Counterions x⁻	Polymer	Abreviation	Tg/°C	$T_{\ominus}$/°C	Mol.% X
I	 "EO"		I-10-Me-EO	111°C	270	97
II	 "MeY"	- " -	I-10-Me- MeY	115°C	272	97
III	 "Crl"	- " -	I-10-Me-Crl	137°C	-	96
IV	- " -		I-6,10$_{\text{stat}}$-Me-Crl	163°C	-	90
V	- " -		S-6,10$_{\text{stat}}$-Me-Crl	76,5°C	-	98
VI	- " -		I-6-Me-Crl	178°C	-	98
VII			I-Do,Pip-Me- MeY	162,5°C	253	97
VIII	 "APX"	- " -	I-Do,Pip-Me-APX	>Te	228	95
IX	 "CrMMO"	- " -	I-Do,Pip-Me-CrMMO	200	242	89

I-6-Me-Crl. The increase of Tg depends also on the stiffness of the polymer chain and on the divalent counterions e.g. APX, CrMMO (see Table I). Glass transition temperature in ionic polymers depends to a large extent on the coulombic interaction between anion and cation which control mobility of they polymer chain. In the case of our polyelectrolytes Tg depends on the strength of coulombic forces between dye anions and positively charged N^+ or S^+ atoms in the polycation chain. At temperatures above Tg the energy of counterions is high enough to leave the coordination sphere of the cation. The relationship between Tg and electrostatic work which must be done in this process was presented by Eisenberg[5].

The considerable difference in Tg values for polyelectrolytes I-6,10_{stat}-Me-Crl and S-6,10_{stat}-Me-Crl (Tg equal to 163 and 76.5° respectively) can be explained taking into account the difference in electrostatic work to be done to separate the anion of Cresol-Red from the cations N^+ or S^+ in the polymer chains. Due to the bigger size and much higher polarizability of the S^+ as compared with N^+ [6] the electrostatic force bounding the anion is much bigger in the latter case which results in a higher Tg value. Lower Tg values were also found for all polysulphonic salts with inorganic anions ; BF_4^-, PF_6^-, SbF_6^-, BPh_4^- [7]. The use of difunctional counterion increases the interaction of the anionic dye with the cation, increases stiffness of the polymer chain leading to the increase in Tg.

The decrease of electrostatic interactions can also explain the decrease of Tg caused by the solvent residue. It is very difficult to obtain solvent-free materials from DMF or DMSO even by prolonged drying at 80°C in vacuum. For I-10-Me-EO obtained in the traditional way (in the water-methanol system) by 97 mol% of Ethyl Orange Tg was equal to 111°C but for this polymer obtained in DMF it was 81°C, and in DMSO 74°C. The amount of remaining DMF or DMSO is estimated to be about 2% w/w.

The influence of remaining solvent in PEL results not only in changes of Tg but also in their dielectric behaviour (which will be discussed in a separate paper). Dipolar molecules of DMF and DMSO remaining in PEL solvate ionic groups in a similar way as it was found in the case of water[8]. The local dielectric constant of the polymer will be increased in such a case and coulombic interactions between the ions will be reduced. This effect is more pronounced when the dielectric constant (ε) of the solvent is higher. For the same polyelectrolyte with traces of DMSO (ε = 48.9) Tg is lower then in the case of DMF (ε = 36.7)

CONCLUSIONS

1. Glass transition temperature of polyelectrolyte glasses can be controlled in a broad range by proper choice of different ionic polymers and almost unlimited choice of organic counterions.
2. Glass transition temperature for discussed systems can also be controlled by the degree for the exchange of counterions to anionic dyes.
3. A considerable decrease of the glass transition temperature of polyelectrolyte glasses with anionic dyes is caused by a small residue of the solvent used for synthesis of film casting.

ACKNOWLEDGEMENTS

The authors are grateful to Dr.J.K.Jeszka for discussion and critical reading of the manuscript.

REFERENCES

1. A.C.Cope and E.R.Trumbell, "Organic Reactions" ,vol 11, Willey and Sons, New York, 1960, pp. 317-493.
2. F.Kremer, L.Dominguez, W.H.Meyer and G,Wegner, Polymer **30** (1989) 2023.
3. W.H.Meyer, J.Pecherz, A.Mathy and G.Wegner, Adv.Mater., 3, 153 (1991).
4. L.Dominguez, W.H.Mayer and G.Wegner, Macromol.Chem.Rapid Commun., 8, 151 (1897).
5. A.Eisenberg and T.Yokoyama, Polym.Preprints,9, 617 (1968).
6. J.Pęcherz and M.Kryszewski, Acta Polym., 34, 19 (1983).
7. J.Pecherz unpublished.
8. T.Tsutsui, R.Tanaka and T.Tanaka, J.Polym.Sci., B14, 2259 (1976).