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Effect of Tacticity of Poly(Methyl Methacrylate) on Conductivity of Poly(Ethylene Oxide)-Poly(Methyl Methacrylate) Blend-Based Polymeric Electrolytest

Z. Florjańczyk^a; K. Such^b; W. Wieczorek^b

^a Institute of Polymer Technology Warsaw University of Technology, Warszawa, Poland ^b Institute of Inorganic Technology Warsaw University of Technology, Warszawa, Poland

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EFFECT OF TACTICITY OF POLY(METHYL METHACRYLATE) ON CONDUCTIVITY OF POLY(ETHYLENE OXIDE)–POLY(METHYL METHACRYLATE) BLEND-BASED POLYMERIC ELECTROLYTES†

Z. FLORJAŃCZYK*

Institute of Polymer Technology
Warsaw University of Technology
ul. Koszykowa 75, 00-662 Warszawa, Poland

K. SUCH and W. WIECZOREK

Institute of Inorganic Technology
Warsaw University of Technology
ul. Noakowskiego 3, 00-664 Warszawa, Poland

ABSTRACT

Polymer electrolytes based on blends of poly(ethylene oxide) (PEO) with various stereoisomers of poly(methyl methacrylate) (PMMA) were studied by means of impedance spectroscopy and DSC. It was found that isotactic poly(methyl methacrylate) (IPMMA)-based electrolytes exhibit ambient temperature conductivities at least one order of magnitude higher than the electrolytes containing other stereoisomers of PMMA. The highest value of room temperature conductivity equal to 9×10^{-5} S/cm was measured for a sample containing 30 wt% IPMMA. The effect observed results from the presence of a flexible amorphous phase in PEO-IPMMA blends which is favorable for fast ionic transport. A small

†Dedicated to Otto Vogl on the occasion of his 65th birthday.

increase of ionic conductivity with decreasing molecular weight of the added atactic poly(methyl methacrylate) was also observed.

INTRODUCTION

High ionic conductivity is one of the most desired properties of solid polymeric electrolytes in respect to the possibility of their application in energy storage systems working at ambient temperatures. Poly(ethylene oxide) (PEO) of high molecular weight is the most commonly used matrix in these systems, and a number of methods were applied to modify its structure in order to achieve highly conductive amorphous electrolytes. Among them, the formation of PEO blends with other macromolecule hosts seems to be a very promising possibility due to its simplicity, wide thermal stability range of products obtained, and their good mechanical properties. In our previous studies [1, 2], PEO blends with high molecular weight atactic poly(methyl methacrylate) (APMMA) complexed with alkali metal salts were examined.

It was found by us that electrolytes obtained from solvent-cast blends exhibited rather moderate conductivity in the 10^{-7} to 10^{-6} S/cm range at ambient temperatures. However, their conductivity increases significantly (1–2 orders of magnitude) after the addition of PEO-PMMA grafted copolymers which act as internal plasticizers.

The main goal of the present paper is to examine the effect of the tacticity of PMMA on the conductivity of electrolytes comprised of solvent-cast PEO-PMMA blends and LiClO_4 . Some data concerning the effect of the molecular weight of PMMA are also presented.

EXPERIMENTAL

PMMA samples of various tacticities were prepared according to procedures described elsewhere [3–5]. Their microstructure was characterized by ^1H NMR. The results of the NMR studies as well as molecular weights of the prepared PMMA are summarized in Table 1. In a later part of the paper, PMMAs with P_m values (P_m = probability of the meso addition leading to the same configuration on two neighboring pseudoasymmetric carbon atoms) equal to 0.82 are called isotactic (IPMMA) and those equal to 0.11 are called syndiotactic (SPMMA). Samples of PMMA obtained by free radical polymerization at 60°C of P_m 0.22–0.24 and of Bernoullian-type triad distribution are called atactic (APMMA).

PEO-PMMA- LiClO_4 electrolytes were obtained by dissolution of solid components in a carefully dried acetonitrile–dichloromethane mixture. The solution was cast onto a flat glass or Teflon substrate, and solvent was evaporated in an evacuated dessicator. All solid reagents were dried by prolonged heating under reduced pressure at about 100°C prior to dissolution. All the experiments were carried out under vacuum or in an inert gas atmosphere. The above-described procedure leads to the preparation of electrolytes in the form of 50–100 μm thick films. For the synthesis, PEO ($M_w = 5 \times 10^6$ g/mol) (Polysciences) and LiClO_4 (Fluka, reagent grade) were used. Solvents were distilled twice over Molecular Sieves type 4A before

TABLE 1. Characteristics of PMMA Used

Isomer ^d	$M_n \times 10^{-4}$ g/mol	Triad mol fraction ^a			P_m^b
		X_{mm}	X_{mr}	X_{rr}	
Isotactic PMMA	1.5	0.80	0.03	0.17	0.82
Syndiotactic PMMA	2.0	0.01	0.22	0.77	0.11
Atactic PMMA	2.8	0.08	0.40	0.52	0.24
Atactic PMMA ^c	2.8	0.078	0.403	0.518	
Atactic PMMA	13.0	0.05	0.34	0.61	0.22
Atactic PMMA ^c	(13.0)	0.048	0.344	0.608	

^a X_{mm} = isotactic, X_{mr} = heterotactic, X_{rr} = syndiotactic.

^bProbability of mes addition.

^cCalculated according to Bernoullian statistics for the given P_m .

^dMolecular weights of PMMA isomers were determined by viscometric experiments.

use. The electrolytes were annealed at room temperature for 30 days before DSC and conductivity measurements.

Conductivities of the studied electrolytes were calculated from impedance spectroscopy data by applying the NLSF (nonlinear least-squares fitting) procedure. Alternating current impedance experiments were performed in the frequency range from 5 Hz to 500 kHz by applying stainless steel blocking electrodes. The measurements were carried out in the temperature range from room temperature to 100°C. Calorimetric experiments were performed on a UNIPAN 605 DSC apparatus in the temperature range from -90 to 150°C. The heating rate was equal to 2 and to 5°/min in the temperature range -90 to 0°C and 0 to 150°C, respectively. DSC curves were analyzed by a special computer program, and T_g values were calculated as the temperature corresponding to 50% of the transition. The ¹H-NMR spectra were recorded in CDCl₃ on a Bruker AM 300 spectrometer.

RESULTS AND DISCUSSION

Changes of the conductivity versus reciprocal temperature for blends of PEO with IPMMA, SPMMA, and APMMA of low molecular weight doped with LiClO₄ (10 mol% in respect to the ethylene oxide monomeric unit) are shown in Figs. 1, 2, and 3. The concentration of PMMA in blends are equal to 20, 30, and 40 wt%. The highest values of ambient temperature conductivity are usually found for samples containing 30 wt% of the added PMMA. As can be seen from Fig. 4 and Table 2, the conductivity increases in the order APMMA < SPMMA < IPMMA in respect to the kind of stereoisomer used, and for the PEO-IPMMA(30 wt%)-LiClO₄ system it reaches the value 9×10^{-5} S/cm at 25°C.

In the temperature region lower than the melting point of pure crystalline PEO (~65°C), the conductivities of electrolytes based on blends containing 30 wt% PMMA are higher than that for the pristine PEO-LiClO₄ system. At temperatures exceeding the melting point of PEO, crystalline phase SPMMA and APMMA im-

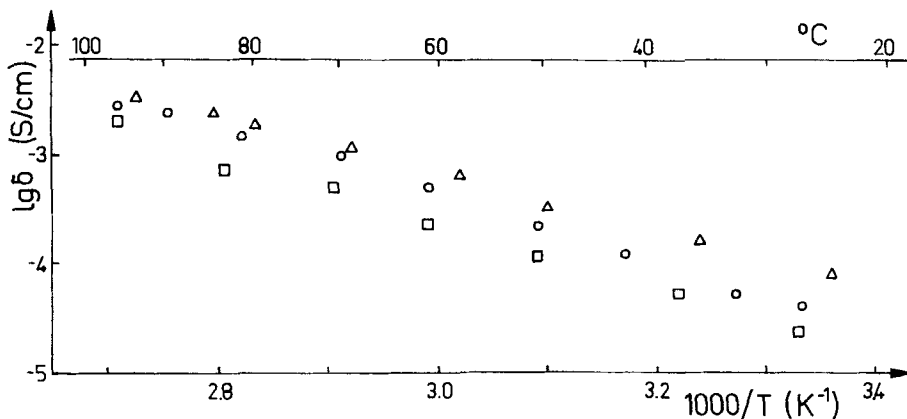


FIG. 1. Changes of ionic conductivity versus reciprocal temperature for PEO-IPMMA blend-based electrolytes doped with LiClO_4 (10 mol% in respect to ethylene oxide monomeric units concentration). Samples of various concentration of IPMMA in blend. (○): 20 wt% IPMMA. (△): 30 wt% IPMMA. (□): 40 wt% IPMMA.

peded the conductivity. However, the conductivity of the PEO-IPMMA- LiClO_4 system is higher than of PEO- LiClO_4 electrolytes up to almost 100°C (the maximum temperature applied).

In order to explain the observed phenomena, the PEO-SPMMA- LiClO_4 and PEO-IPMMA- LiClO_4 systems were subjected to DSC studies. Examples of DSC curves are shown in Fig. 5. The thermograms of the electrolytes studied present a

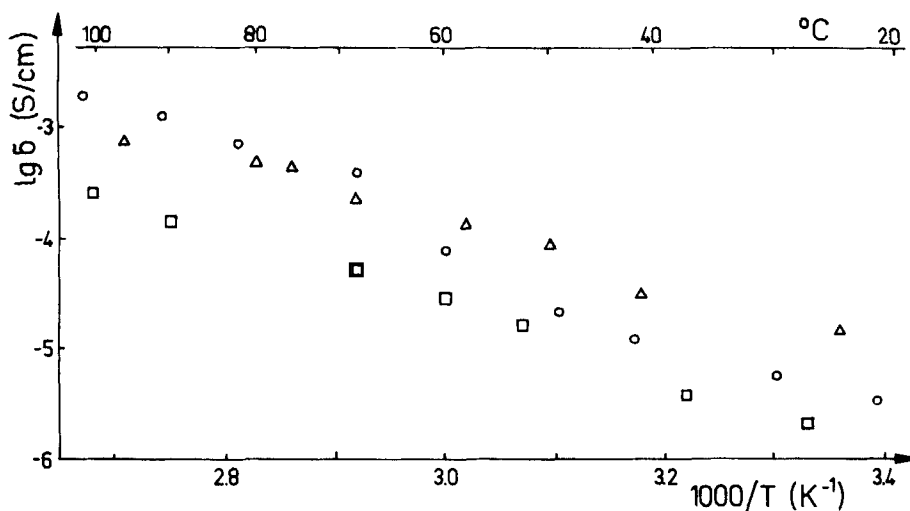


FIG. 2. Changes of ionic conductivity versus reciprocal temperature for PEO-SPMMA blend-based electrolytes doped with LiClO_4 (10 mol% in respect to ethylene oxide monomeric units concentration). Samples of various concentration of SPMMA in blend. (○): 20 wt% SPMMA. (△): 30 wt% SPMMA. (□): 40 wt% SPMMA.

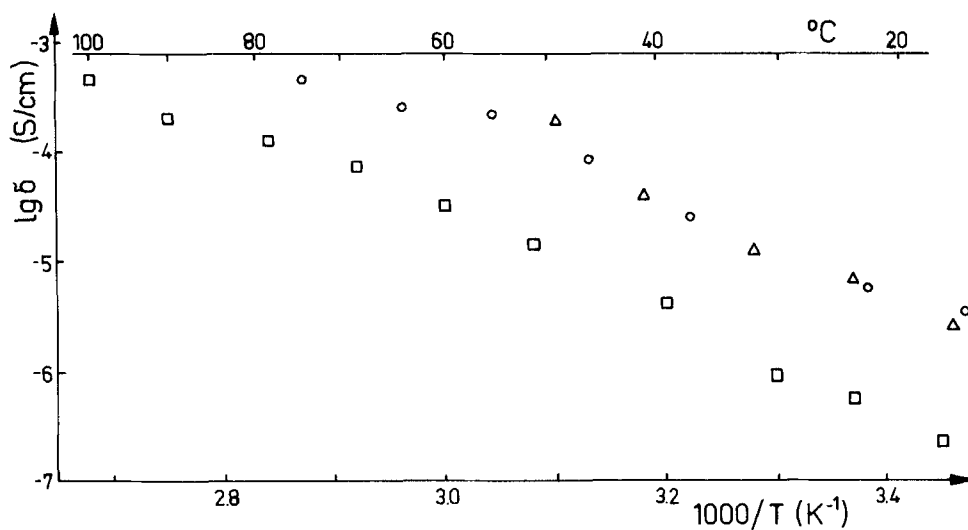


FIG. 3. Changes of ionic conductivity versus reciprocal temperature for PEO-APMMA blend-based electrolytes doped with LiClO_4 (10 mol% in respect to ethylene oxide monomeric units concentration). Samples of various concentration of APMMA in blend. M_w of APMMA is equal to 2.8×10^4 g/mol. (○): 20 wt% APMMA. (△): 30 wt% APMMA. (□): 40 wt% APMMA.

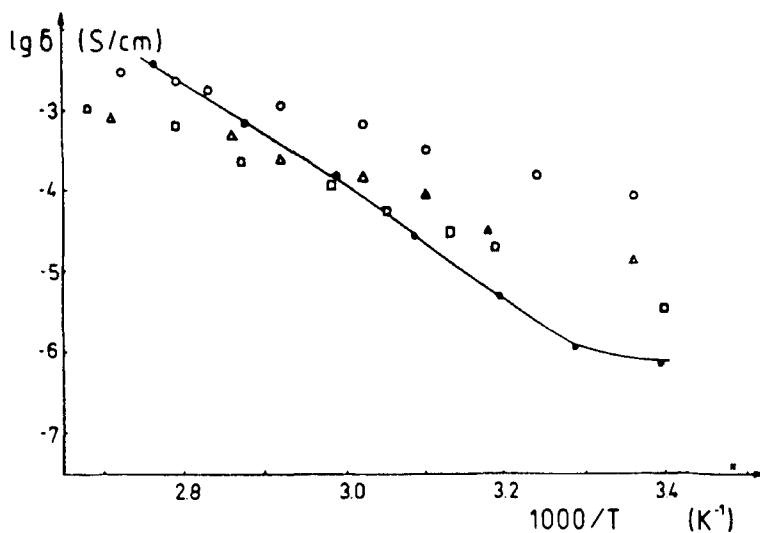


FIG. 4. Comparison of changes of conductivity versus reciprocal temperature for PEO-PMMA blends containing PMMA of various tacticities. Concentration of PMMA in blend is equal to 30 wt%. All samples are doped with LiClO_4 (10 mol% in respect to ethylene oxide monomeric units concentration). (○): Electrolyte containing IPMMA. (△): Electrolyte containing SPMMA. (□): Electrolyte containing APMMA.

TABLE 2. Ionic Conductivity of Some PEO/PMMA/LiClO₄ Electrolytes at Ambient Temperature^a

PMMA isomer	$M_n \times 10^{-4}$ g/mol	Temperature, K	Conductivity, S/cm
Isotactic PMMA	1.5	298	9.0×10^{-5}
Syndiotactic PMMA	2.0	294	1.4×10^{-5}
Atactic PMMA	2.8	294	5.7×10^{-6}
Atactic PMMA	3.8	294	3.5×10^{-6}
Atactic PMMA	9.0	292	2.1×10^{-6}
Atactic PMMA	13.0	293	1.3×10^{-6}

^aConcentration of PMMA in blends is equal to 30 wt% concentration of the dopant salt (LiClO₄) which is equal to 10 mol% in respect to ethylene oxide monomeric units.

clear T_g below 0°C for all the compositions tested and broad endothermic peaks in the range 55–130°C. These peaks are attributed to the melting of crystalline PEO and PEO-LiClO₄ complex phases. One can observe (Table 3) that IPMMA electrolytes contain an amorphous phase of very low T_g (–57 to –45°C). These T_g values are only slightly higher than that measured for pure PEO (–59°C) and much lower than the T_g values predicted by the Fox equation for blends miscible at a random level. This fact seems to suggest that the PEO-IPMMA system is separated into two phases, one of low T_g rich in PEO and the other rich in IPMMA. The T_g for the latter phase should appear at the higher temperature range and is probably masked by the melting peaks of crystalline phases [6]. It should be noted that the T_g value of the PEO-rich phase is lower than that measured for the PEO-LiClO₄ electrolyte (~ –25°C). This indicates that the addition of IPMMA greatly reduces the cross-linking effect of the added salt, which usually leads to lowering the flexibility of the conducting amorphous phase and to an increase of the T_g value. One can assume that in PEO-IPMMA-LiClO₄ electrolytes, the conductive flexible regions of amorphous PEO are separated by a nonconductive polymer which lowers the probability of coordination of neighboring PEO chains around the lithium cation. This results in an increase of mobility of the solid polymeric solvent and, hence, in higher conductivity values.

It was previously reported by Silvestre et al. [6] that SPMMA and APMMA are more miscible with PEO than IPMMA. It was supposed that for blends containing up to 40 wt% of SPMMA or APMMA crystallized at 48°C, one homogeneous amorphous phase was present. According to theoretical predictions [7], these systems should be miscible in the amorphous phase in the temperature range 0–200°C. However, no experimental data supporting the above considerations are available. As can be seen from Table 3, the T_g values for electrolytes containing SPMMA are higher than those for PEO-IPMMA blend-based electrolytes. This probably results from the higher content of methacrylic polymer in the blend and higher T_g value for SPMMA (127°C). The T_g values obtained for electrolytes containing SPMMA are very close to those reported for pristine PEO-LiClO₄ systems. Thus, one can expect that PMMA isomers of high syndiotactic triad concentration will not improve the

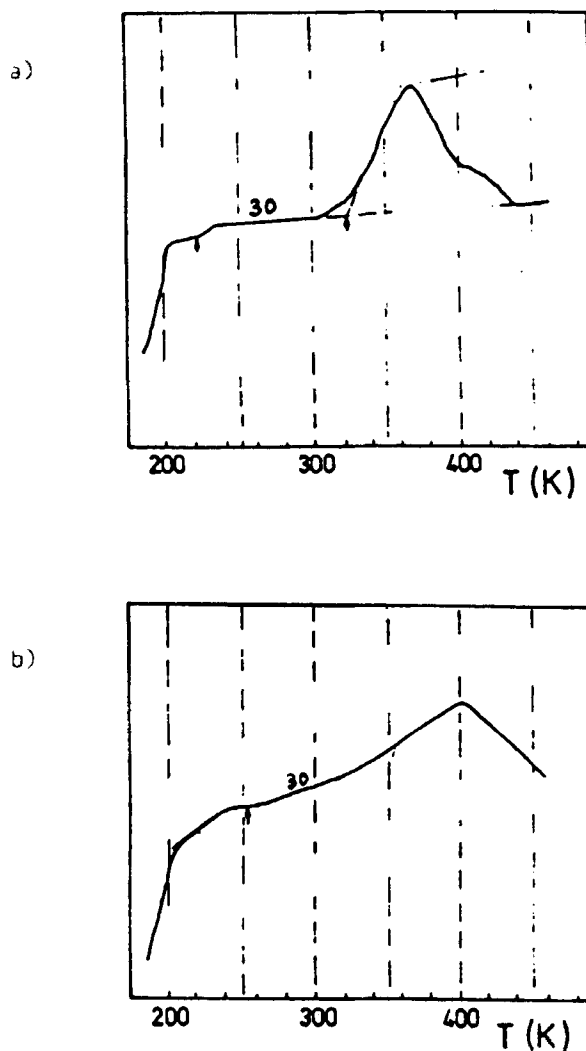


FIG. 5. DSC curves registered for (a) $(\text{PEO})_{10}\text{LiClO}_4\text{-IPMMA}$ (30 wt%) and (b) $(\text{PEO})_{10}\text{LiClO}_4\text{-SPMMA}$ (30 wt%).

flexibility of the conducting phase. In fact, as a nonconducting component of an amorphous phase, it should make ion transport more difficult, which is clearly visible above the melting point of the PEO crystalline phase. This also seems to be a reason for the lowered conductivity of electrolytes containing more than 30 wt% of PMMA.

Improvement in the ambient temperature conductivities of PEO-APMMA and PEO-SPMMA blend-based electrolytes in comparison to PEO based systems may be attributed to their lower degree of crystallinity. Unfortunately, the shape of the melting peaks, as well as lack of data concerning the melting heat of the pure crystalline PEO- LiClO_4 complex phase, make it impossible to establish the degree

TABLE 3. Glass Transition Temperature (T_g) Obtained from the DSC Experiments for PEO-PMMA-LiClO₄ Electrolytes

PMMA isomer	Concentration of PMMA,		
	wt%	T_g , °C	T_g^a , °C
Isotactic PMMA	20	-57	-43
Istactic PMMA	30	-53	-33
Isotactic PMMA	40	-45	-23
Syndiotactic PMMA	20	-27	-37
Syndiotactic PMMA	30	-24	-24
Syndiotactic PMMA	40	-21	-10

^aGlass transition temperature calculated from the Fox equation for undoped PEO-PMMA blends.

of crystallinity of PEO-PMMA blend-based electrolytes on the basis of DSC data.* However, it is clearly seen that samples containing SPMMA are less crystalline than those containing IPMMA. A similar effect was previously observed for undoped blends [6, 8] and was explained by different mobilities of crystallizable chains. The higher diffusion rate of chain segments and hence the rate of crystallization and reorganization for PEO-IPMMA blends gives PEO the possibility of crystallizing in a more complete way. However, the higher room temperature conductivity of

*The results obtained enable us to make a rough estimate of the content of the crystalline PEO phase. These values are in the ranges 0–15% and 20–40% for electrolytes containing SPMMA and IPMMA, respectively.

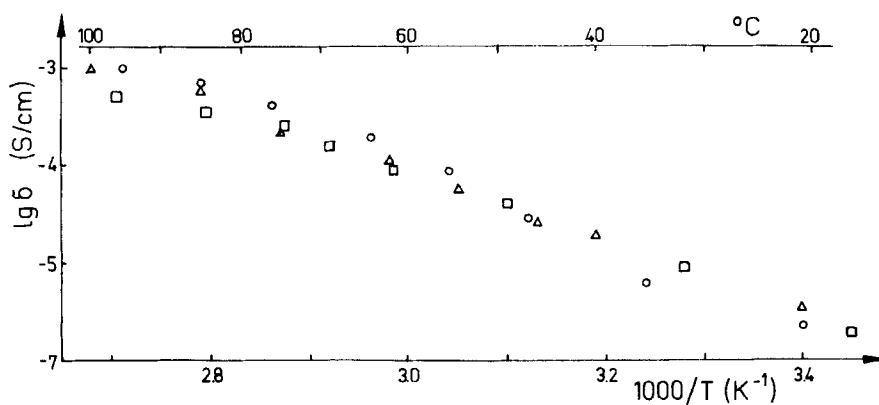


FIG. 6. Changes of ionic conductivity versus reciprocal temperature for PEO-APMMA blend-based electrolytes doped with LiClO₄ (10 mol% in respect to ethylene oxide monomeric units concentration). Samples of various concentrations of APMMA in blend. M_w of APMMA is equal to 3.8×10^4 g/mol. (○): 20 wt% APMMA. (△): 30 wt% APMMA. (□): 40 wt% APMMA.

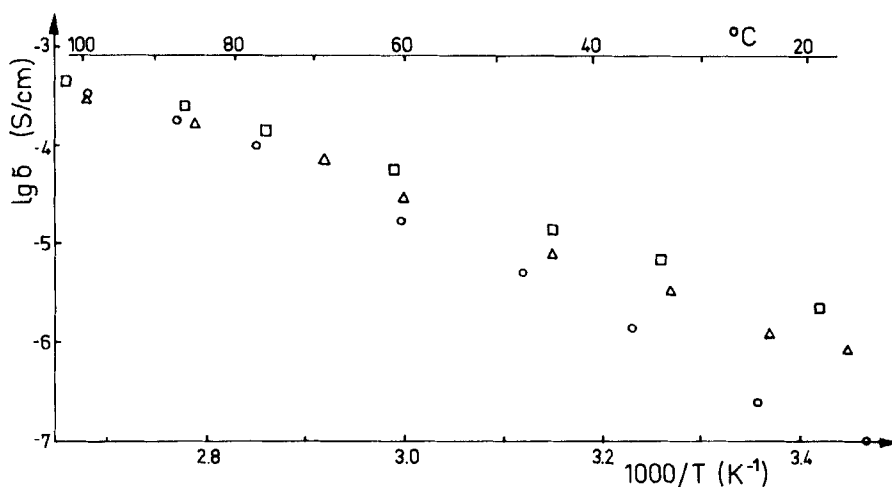


FIG. 7. Changes of ionic conductivity versus reciprocal temperature for PEO-APMMA blend-based electrolytes doped with LiClO_4 (10 mol% in respect to ethylene oxide monomeric units concentration). Samples of various concentrations of APMMA in blend. M_w of APMMA is equal to 9.0×10^4 g/mol. (○): 20 wt% APMMA. (□): 30 wt% APMMA. (△): 40 wt% APMMA.

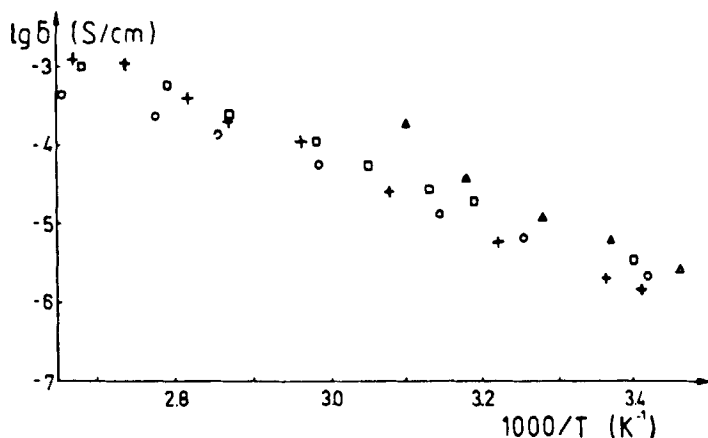


FIG. 8. Comparison of changes of conductivity versus reciprocal temperature obtained for PEO-APMMA- LiClO_4 electrolytes containing APMMA of various molecular weights. Concentration of APMMA in blend is equal to 30 wt%. All samples are doped with LiClO_4 (10 mol% in respect to ethylene oxide monomeric units concentration). (+): APMMA of M_w equal to 1.3×10^5 g/mol (commercially available polymer additionally purified by us before experiments). (○): APMMA of M_w equal to 9.0×10^4 g/mol. (□): APMMA of M_w equal to 3.8×10^4 g/mol. (△): APMMA of M_w equal to 2.8×10^4 g/mol.

PEO-IPMMA-LiClO₄ electrolytes indicates that conductivity in the systems studied is governed by the flexibility of the amorphous phase rather than by the ratio between the crystalline and amorphous regions. The difference in the amorphous phase contents may be the reason for the higher conductivity of PEO-SPMMA-LiClO₄ systems compared with PEO-APMMA-LiClO₄ electrolytes since it is known that undoped APMMA blends are more crystalline whereas the flexibilities of the PMMA isomers are very close [6].

As can be seen from Table 1, there are small differences in the molecular weights of the PMMA isomers studied. In order to examine whether we can invoke these differences in a discussion of tacticity effects on the conductivity of PEO-PMMA blends, polymer electrolytes containing APMMA with molecular weights ranging from 9×10^4 to 2.8×10^4 g/mol were studied. Changes in the conductivity versus the reciprocal temperature for these electrolytes are shown in Figs. 3, 6, and 7. For each of the systems studied, the conductivity exceeded 10^{-7} S/cm at room temperature. The best conductivity results were obtained for samples containing 30 wt% PMMA. Figure 8 and Table 2 show the conductivities obtained for electrolytes containing PMMAs of various molecular weights. As can be seen, the room temperature conductivity increases with decreasing molecular weight of the added PMMA. However, it is evident that the effect of the PMMA molecular weight on the conductivity of PEO-PMMA blend based electrolytes is not as pronounced as the effect of the PMMA tacticity.

CONCLUSIONS

The main conclusion of this paper is that blends of PEO-LiClO₄ electrolyte with IPMMA yield better conducting polymer electrolytes than do those with SPMMA and APMMA. The explanation for this is not easy due to the complexity of the system: Partial mixing of PMMA and PEO which might change upon the addition of LiClO₄. However, the low T_g of the prepared electrolytes and the lowering of the crosslinking effect of the added salt seem to be crucial factors. In the case of electrolytes containing SPMMA and APMMA, the increase of conductivity noticed below the melting point of the crystalline PEO phase may be attributed to the lower degree of crystallinity of the systems in comparison to that of the pristine PEO-LiClO₄ electrolyte.

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