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Study of polymer blends of poly(acetylene) with poly(methyl methacrylate) and methyl methacrylate-butadiene-styrene copolymer

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Summary

Electroactive polymer blends of polyacetylene (PA) with poly (methyl methacrylate) (PMMA) or methyl methacrylate-butadien-styrene (MBS) copolymer were prepared in situ as free-standing films or powders by polymerization of acetylene in the presence of PMMA or MBS-copolymer, using Luttinger's catalyst. Blends of different composition were studied by infrared spectroscopy and electrical conductivity measurements. Environmental stability of pristine and doped PA was improved to some extent in the presence of PMMA.

Introduction

Due to the unique electrical properties polyacetylene is one of the most widely studied conjugated polymers. Usually it is prepared as a film or powder which are insoluble and infusible. The intractability and instability in air have impeded the practical applications of this material. Blending of PA with a polymer with desirable physical and mechanical characteristics is one of the routes to overcome this serious obstacles.

It is known (1,2) that polymerization of a monomer in a polymer matrix is useful approach to the preparation of new materials in situ. It provides the possibility for more intimate mixing of the components, compared with the mechanical blending, especially in view of the incompatibility of most polymers.

Blends of PA with polyethylene (PE), polystyrene (PS) (3-5), polybutadiene (PB) (6,7) and ethylene-propylene-diene (EPD) terpolymer (8) of good mechanical properties have been prepared in situ, polymerizing acetylene in the matrix of corresponding polymer. They preserve the high electrical conductivity of the PA component after doping.

Oxidation stability of the blends upon air exposure is improved to some extent for some of the polymer matrices used - PE (3) and EPD terpolymer (8), while the poor oxygen barrier provided by PB matrix precludes any long range stability (6).

In previous investigations polymer blends were prepared by polymerization of acetylene in a film of matrix polymer impregnated with Ziegler-Natta catalyst. It is known (9,10) that in contrast to Ziegler-Natta catalyst,

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Luttinger's catalyst system consisting of $NaBH_4$ and $Co(NO_3)_2$ works in polar media without elimination of moisture. This simplified the experimental technique and also allows polar polymers to be used as a component of the polymer blends.

In the present work the possibility of preparation of polymer blends in situ by polymerization of acetylene using Luttinger's catalyst in the presence of PMMA and MBS copolymer was studied. Having in mind substantially lower oxygen permeability (11) of PMMA compared to PE and EPD terpolymer, it could be supposed that the stability of PA upon air exposure will be improved in higher extent in the presence of PMMA.

Experimental

-Preparation of polymer blend PA-PMMA in situ by polymerization of acetylene in the presence of PMMA

Solution of 0,5 g PMMA in 5 ml butanon-2 was added into the solution of 0,1 g $NaBH_4$ in 4 ml butanon-2. Solution of 0,01 g $Co(NO_3)_2$ in 1 ml butanon-2 was prepared separately. The two solutions were cooled down to -80° C, mixed together and poured into the reaction flask precooled to -80° C. Polymerization of acetylene in the slowly rotating flask and isolation of the films PA-PMMA were performed as desribed in previous communication (12). Films of thickness about 10-80 μm containing 60-67% PA and 33-40% PMMA were obtained.

-Preparation of polymer blend PA-MBS in situ by polymerization of acetylene in the presence of MBS copolymer

Aqueous latex of MBS copolymer (composition: 50 mass% elastomer, 25 mass% methyl methacrylate units and 25 mass% styrene units) was coagulated by ethanol; 8,5 g suspension containing 3,5 g of MBS copolymer was obtained. 70 ml of ethanol were added to the suspension and after cooling to -40° C catalyst solution consisiting of 0,2 g $NaBH_4$, 0,1 g $Co(NO_3)_2$ and 30 ml ethanol precooled to -40° C was added.

A slow streem of acetylene passing first through a coil cooled at -40° C was allowed to pass through the reaction mixture while stirring and keeping the temperature at -40°C. The precipitate obtained containing 87,5 mass% MBS and 12,5 mass% PA was filtered in argon. In order to prepare a film, 0,300 g of the product containing 0,170 g MBS and 0,024 g PA was wetted by ethanol, blended with 2 ml 5 mass% solution of PMMA in butanon-2 and casted onto Teflon foil. Solvent was eliminated by blowing of argon gas and a film of thickness about 700 μm was obtained.

- Preparation of PA and PA-PMMA films.

Cis-rich PA film of thickness about 10-20 μm and PA powder were prepared according to the method described in a previous paper (12). Film of powdered PA and PMMA was prepared by mixing of 0,12 g PA with 1 ml 5 mass% solution of PMMA in butanon-2 and casting onto Teflon foil. Solvent was eliminated by blowing of argon gas and film of thickness about 300 μm was obtained.

- Doping

Samples were immersed in a saturated iodine /pentane solution for 24 h or 48 h, followed by washing with pentane until clear rinse and then pumping in vacuo for 24 h. Dopant concentration was determined by mass uptake.

- Measurements

Electrical conductivity of doped samples was measured by the four-probe technique immediately after doping and after exposure to air at room temperature.

I.r. spectra of PA and PA-PMMA films were taken on Specord M80 (Karl Zeiss) immediately after preparation and after exposure to air at room temperature.

Results and Discussion

1. Polymer blends PA-PMMA

Films PA-PMMA (Table 1,Nō2) prepared in situ by polymerization of acetylene in the presence of PMMA are found to be quite flexible, tough and macroscopically homogeneous. They are more reddish compared to films of PA obtained under the same conditions. As seen from Fig.1, I.r. spectrum of the blend is a simple superposition of the spectra of the two components, with no observable frequency shifts in the absorption bands. This is an indication for the absence of molecular mixing and specific intermolecular interactions between the two components.

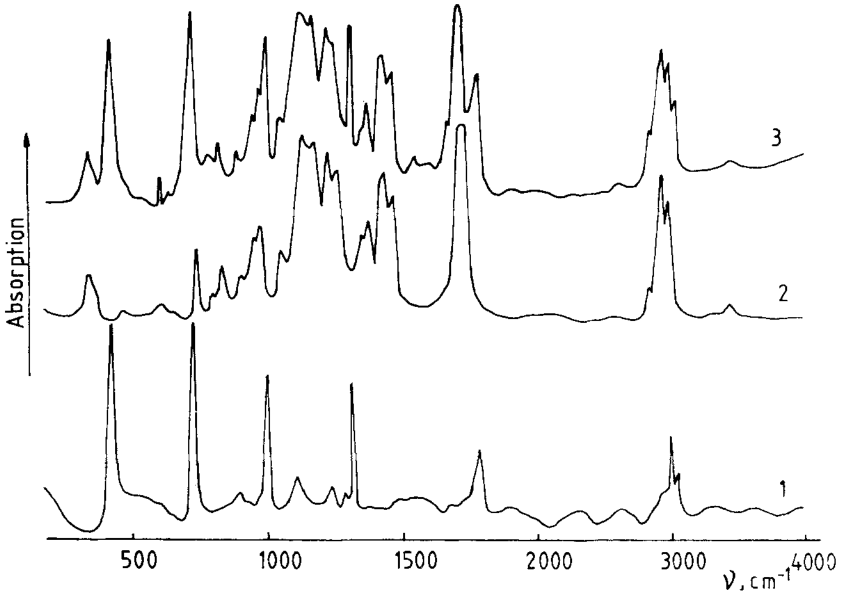

Fig. 1. Infrared spectra of (1): PA; (2): PMMA and (3): PA-PMMA blend.

As the acetylene polymerization was performed at low temperature, cis-isomer dominates in the blend.Plot of cis-content, determined by the procedure of Ito et al.(13) vs. exposure time of PA and PA-PMMA films to air at room temperature, is shown in Fig.2. As seen,the rate of the "oxygen catalized" cis-trans isomerization of PA (14,15) during the air exposure is lower in the presence of PMMA and is negligible after 170 h.

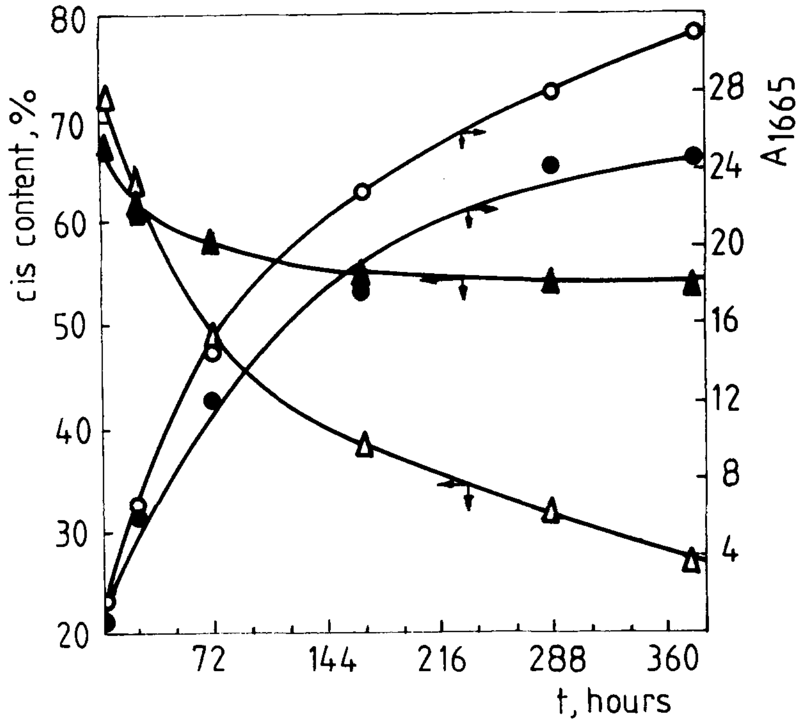

Fig. 2. Cis-PA content and absorbance of the band at 1665 cm^{-1}vs. exposure time of PA and in situ prepared blend PA-PMMA in air at room temperature;/ Δ ,o: PA; ▲ ,●: PA-PMMA/

It is known that cis-trans isomerization of PA proceeds by rotation of chain segments around single bonds(16). It was supposed (17) that models for the isomerization mechanism (16,18) based upon isolated chains are unrealistic. The host crystalline lattice of PA imposes limitations on the chain segments rotation. It is quite plausible to assume that the decreasing in the rate of isomerization in the presence of PMMA is due to structural reasons which have to be further studied and elucidated.

Stability of pristine PA in the polymer film PA-PMMA prepared in situ, during exposure to air at room temperature was followed by the change of absorbance of the i.r. band at 1665 cm^{-1}, assigned to α,β - unsaturated keton (19)(Fig.2). Stability of iodine doped PA in the same film was followed by conductivity measurements (Fig.3). It is seen that stability in air of pristine and doped PA increases to some extent in the presence of PMMA, due probably to the very low oxygen permeability of PMMA. Alternatively, increased stability of PA obtained in the presence of PMMA, could be ascribed to higher viscosity of the reaction medium, supposed as one of the reasons of higher stability of Naarmann PA (21) compared to the conventional Shirakawa PA.

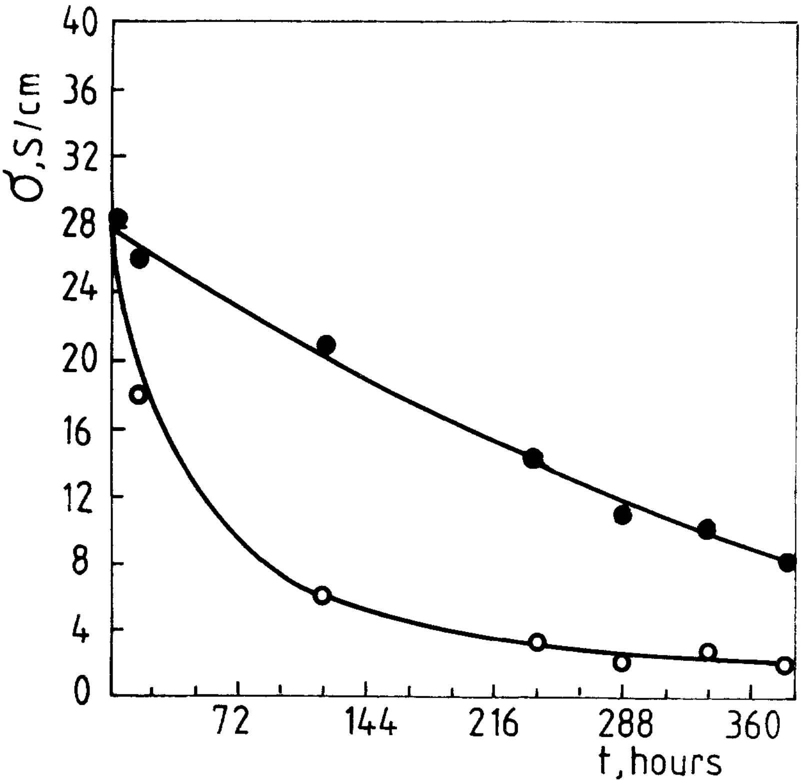

Fig. 3. Conductivity of doped PA and in situ prepared blend of PA-PMMA vs. exposure time in air at room temperature: /o: PA; ●: PA-PMMA/.

As evident from Fig.3, initial conductivity values of doped PA and doped PA-PMMA films are equal. This is an indication that in the polymer blend PA-PMMA prepared in situ, continuous filamentary matrix could be supposed, and electrical properties of the blend are characteristic of PA alone.

2. Polymer blends PA-MBS and PA-MBS-PMMA

Polymer blend PA-MBS prepared in situ by polymerization of acetylene in suspension of MBS-copolymer in water-alcohol mixture, is gel-like product, which results in powdered composition on drying in argon gas. In contrast to the original MBS-component of the blend, it is insoluble and even does not swell in benzene. This is probably due to the encapsulation of MBS particles in a thin coating of PA.

Pressing of the product in gel-like or powdered form results in brittle, macroscopically inhomogeneous films of conductivity $\sim 10^{-13}$ ohm^{-1}. cm^{-1} , which increases up to 10^{-7} ohm^{-1}. cm^{-1} after iodine doping.

Table 1: Composition and conductivity of polymer blends containing polyacetylene

No	Polymer blend	Composition of the blend, mass%			Y in $(CHI_y)_x$		Conductivity S.cm^{-1}	
		PA	PMMA	MBS	doping 24h.	48h.	doping 24h.	48h.
1.	PA	100	-	-	0,16	0,16	10^{1}	10^{1}
2.	PA-PMMA	67	33	-	0,14	0,14	10^{1}	10^{1}
3.	PA-MBS-PMMA	8	33	59	0,10	0,16	10^{-4}	10^{-2}
4.	PA(powder)-PMMA	67	33	-	0,10	0,10	10^{-1}	10^{-1}
5.	PA(powder)-PMMA	8	92	-	0,10	0,10	$<10^{-8}$	

Film of relatively higher quality was casted from mixture of powdered blend PA-MBS with PMMA solution in butanone-2 (Table 1, No3). Having in mind above mentioned possibility for encapsulation of MBS particles in thin PA coating, this film was casted using the same mass ratio (PA+MBS):PMMA, as the ratio PA:PMMA in the film prepared in situ by polymerization of acetylene in the presence of PMMA (Table 1,No2), described in the preceeding section. For the sake of comparison two films were casted from mixture of powdered PA and PMMA solution as follows:

(a) using the same mass ratio PA:PMMA as in the blend No2 in Table 1 prepared in situ (Table 1,No4); and

(b) using the same mass fraction of PA as in the blend No3 in Table 1 (Table 1,No5).

Data on the composition, doping level of PA and electrical conductivity are presented in Table 1. As seen, except for the blend PA-MBS-PMMA (No3), doping levels and corresponding conductivity values of all the samples do not depend on the immersion time in dopant solution used (24h or 48h). Conductivity of the polymer blend PA-PMMA prepared in situ (No2) is two orders of magnitude higher compared to the blend No4 containing the same mass fraction of powdered PA, but lower doping level. Still lower conductivities were measured for blends NoNo3 and 5 where the mass fraction of conducting component is much lower. Comparing this two blends, however,it is seen that conductivity of the blend PA-MBS-PMMA (No3) is several orders of magnitude higher. Evidently, concentration of PA in the blend No5 is too low the percolation threshold to be reached. At the same mass fraction of the conducting polymer, however, encapsulated in polyacetylene particles of MBS copolymer, due to the higher volume fraction of (PA+MBS) in the blend PA-MBS-PMMA (No3) provide the possibility for the formation of more or less continuous pathway throughout the blend, and corresponding fairly high conductivity value, particularly after 48 h doping,have been reached. This value, however, is 3 orders of magnitude lower than conductivity for the blend No2 with the same mass fraction of PA as mass fraction (PA+MBS) in the blend No3. It is most likely that the real doping level of PA component in the blend PA-MBS-PMMA is considerably lower than the calculated by mass uptake, due to iodine sorption by the MBS copolymer itself. Actually, under the doping conditions used, mass uptake of blank sample of MBS copolymer is more than 10%.

Conclusions

Electroactive polymer materials have been prepared in situ by polymerization of acetylene in the presence of PMMA and MBS copolymer.

Environmental stability of pristine and doped PA is improved to some extent by PMMA due to it's very low oxygen permeability.

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