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Cryochemical synthesis of Mg-containing poly(*p*-xylylene)

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The organomagnesium compounds included in the polymer chain were produced by solid-state photopolymerization of *p*-xylylene at 80 K. The structure of the compounds and features of the obtained polymer are discussed using the infra-red and Raman spectroscopic data. © 1997 Elsevier Science Ltd. All rights reserved.

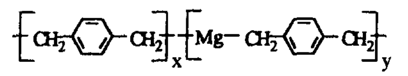
(Keywords: organomagnesium compounds; metal polymer; cryochemical synthesis)

INTRODUCTION

Metal atoms and molecular high-temperature species are useful chemical reagents for the synthesis of various organometallic and inorganic compounds[1,2]. The fabrication technique is known as metal vapour synthesis[3]. Application of this method in polymer science also allows the development of new organometallic polymers and composite materials based on traditional polymers and monomers.

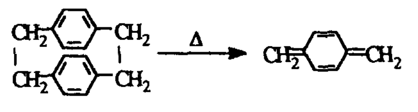
Recently co-condensation of *p*-xylylene (PX) and Mg at 80 K followed by polymerization of the co-condensate of formation of poly(PX) film with the inclusion of organomagnesium compounds has been shown[4]. However almost nothing is known about the structure of this system.

In the present paper the structure of Mg-containing poly(PX) is discussed, based on infra-red (i.r.) and Raman spectroscopy data. It has been established that co-condensation at 80 K produces organomagnesium compounds with Mg–C covalent bonds. As a result of the polymerization the compounds are most likely coupled with poly(PX) units to form a composite structure of the type



EXPERIMENTAL

PX was obtained by gas-phase pyrolysis of *p*-cyclophane (PC)[5]: solid PC was sublimated at 383 K and the vapours were passed through a pyrolitic quartz tube at 873 K. Special spectral measurements showed that under the chosen conditions PC quantitatively converts to PX according to the scheme shown below, without the formation of detectable side products.



In an outlet of the pyrolytic tube the PX vapours were mixed with Mg vapours produced by sublimation of metallic Mg at 673–773 K. The PX-Mg gaseous mixture was deposited onto Si or KRS-5 fastened to a steel cell of an optical cryostat which was cooled to 80 K.

The i.r. spectra were recorded using a Perkin-Elmer 580 spectrophotometer, and the Raman spectra were measured using a Perkin-Elmer MPF-44 spectrometer with an excitation radiation of 5145 Å.

Polymerization was carried out at 80 K using non-filtered irradiation of a high-pressure mercury lamp. The thickness of the deposited polymerized films were measured using a laser interferometer giving values between 1 and 2 μm.

A relative molar Mg-content (X_{Mg}) was evaluated from the Mg–O absorbance band at 450 cm^{-1} after an oxidation of the Mg contained in the polymerized film in air (see below). Specially prepared mixtures of poly(PX) and MgO were used for calibration experiments. According to the spectral data X_{mg} was approximately 0.4.

RESULTS AND DISCUSSION

A typical i.r. spectrum of the film produced by co-condensation of Mg with PX at 80 K is presented in *Figure 1a*. There are absorption bands of the quinonoid molecules of PX at 470 and 870 cm^{-1} in this spectrum[6], but the characteristic band of poly(PX) at 1515 cm^{-1} assigned to the C–C skeletal in-plane vibrations of

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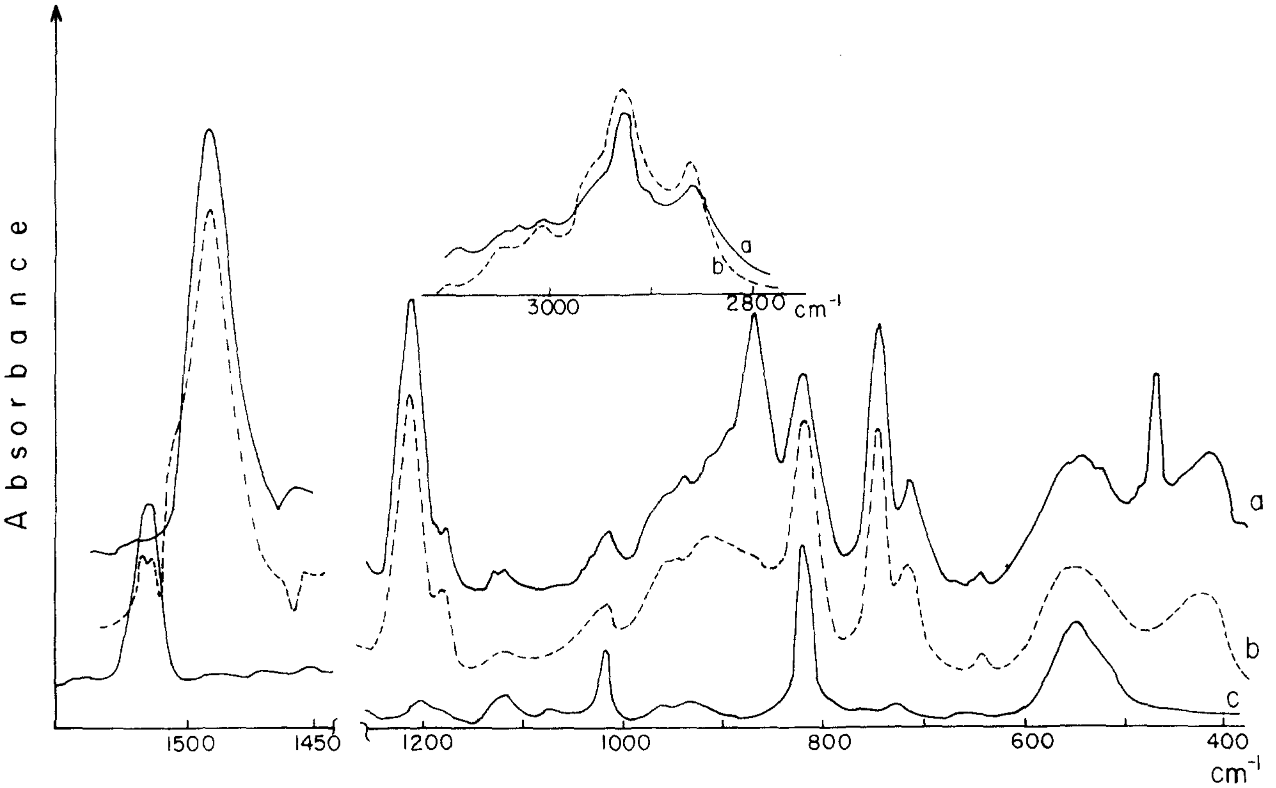
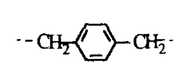


Figure 1 I.r. spectra of the films at 80 K: (a) co-condensate PX with Mg; (b) co-condensate PX with Mg after u.v.-irradiation; (c) poly(PX) obtained by photopolymerization at 80 K

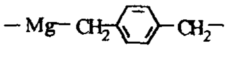
benzene rings in poly(PX) units[7] is absent. So it may be concluded that PX does not polymerize during co-condensation with Mg under the given conditions. But under ultraviolet (u.v.) irradiation the PX in this system polymerizes quantitatively at 80 K[8]; the i.r. bands of PX disappear completely and the i.r. band of poly(PX) at 1515 cm^{-1} can be seen in the spectrum of irradiated film (*Figure 1b*). The other absorption bands shown in *Figure 1a* do not significantly change during u.v. irradiation (compare *Figures 1a* and *1b*) and evidently characterize compounds resulting from the reaction of PX with Mg.

This reaction leads to a transformation of the quinonoid PX into its benzenoid form (PX$_a$)



which is closed to the poly(PX) units, but polarized and slightly deformed under influence of Mg bound to PX$_a$. The strong absorption band at 1480 cm^{-1} (*Figure 1a*) is assigned to the C–C skeletal in-plane vibrations of benzene rings in the obtained Mg-PX$_a$ compounds. A shift of this band to a low-frequency region as compared with the analogous band of pure poly(PX) (*Figure 1c*) appears to be a result of certain deterioration of the benzene ring because of an electron transfer from Mg to PX$_a$. Complexation of PX (model of poly(PX) units) with transition metals or introduction of the electro-donor substitutes into the benzene ring give the same effect[9,10]. Strong absorption bands at 2920 and 2850 cm^{-1} observed in the i.r. spectrum of the PX-Mg co-condensate (*Figure 1a*) are related to stretching C–H vibrations in sp^3-hybridized CH$_2$ groups[11,12]. As noted above, the original films (before u.v. irradiation) do not contain any trace of poly(PX) and hence such CH$_2$-groups probably belong to PX$_a$-Mg compounds. Increasing intensity of these bands during photopolymerization of condensed PX can be accounted for by the formation of new poly(PX) units (*Figure 1b*).

It should be noted that the produced organomagnesium structures are quite stable and begin to deteriorate in vacuum only at temperatures higher than 340 K. Exposure of the polymeric films to air leads to complete oxidative destruction of the compounds: we can see a characteristic wide band of Mg–O stretching vibrations with maximum at 460 cm^{-1} on a background of the poly(PX) spectrum (*Figure 2*), but this does not noticeably affect the position or intensity of the C–H bands. This means that all the CH$_2$ groups in the obtained system including those connected to the Mg have sp^3-hybridization. So the sp^2 to sp^3 rehybridization in our case is caused by not only the electrostatic interaction between PX$_a$ and Mg, but rather results from the Mg–CH$_2$ covalent bond formation in organomagnesium compounds[3], giving rise to the structure (I) shown below:


(I)

According to the literature[10,14,15] the stretching Mg–CH$_2$ vibrations should be revealed in the spectral range of 500–350 cm^{-1}. Thus we believe that the specific absorption band at 410 cm^{-1} (*Figures 1a* and *1b*) characterizes such type of vibrations.

The Mg–CH$_2$ covalent bond in structure I is highly polarized with the electron density of the bond almost entirely shifted to the PX$_a$, with a consequent polarization and some strengthening of the neighbouring

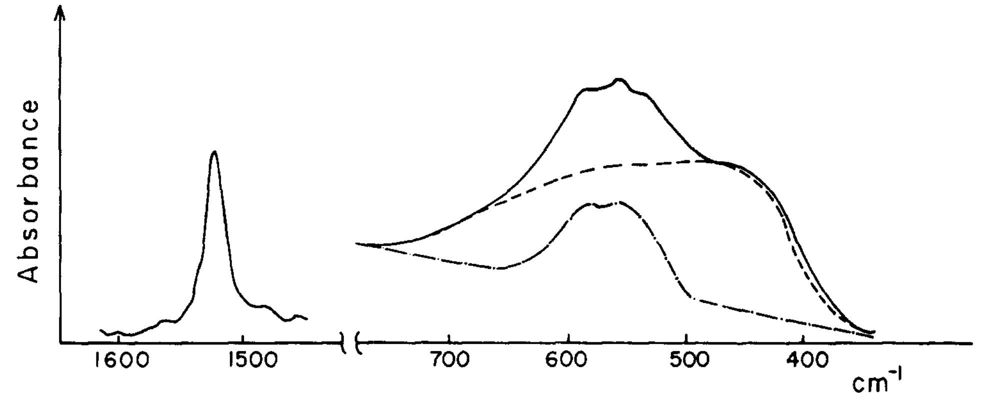


Figure 2 I.r. spectrum of poly(PX) with Mg after annealing in air, the dashed line indicates the MgO spectrum obtained after subtraction of the poly(PX) band

CH_2–benzene ring bond. According to this the strong band at 1210 cm^{-1} in *Figure 1a* is to be assigned to stretching vibrations of the polarized bonds of $MgCH_2$-benzene ring. The analogous band in the i.r. spectrum of poly(PX) is very weak and lies at 1200 cm^{-1} (*Figure 1c*). Localization of a negative charge on the CH_2 into Mg–CH_2 bond also causes deformation vibrations of C–H bands, and the corresponding absorption bands of the i.r. spectrum are much more intensive and shifted to a low frequency. By analogy with diallylmagnesium the intensive i.r. absorption band at 740 cm^{-1} can be assigned to rocking CH_2 vibrations in $MgCH_2$ groups of structure I[14].

Raman spectral data are presented in *Figure 3*. The laser radiation used in the Raman spectroscopy provoked polymerization of the original monomer system. Therefore, only Raman spectra of the polymerized films were recorded. The intense line at 1600 cm^{-1} observed in the Raman spectrum of Mg-containing films (*Figure 3a*) is caused by an active mode of in-plane skeletal benzene ring's C–C vibrations in organomagnesium structures, whereas the analogous line of pure poly(PX) lies at 1620 cm^{-1}. This spectral shift is similar to those of the corresponding i.r. absoption band (see above). The line from the poly(PX) units in the Raman spectra of the polymerized film with Mg appears as a shoulder, near 1600 cm^{-1}, at the line at 1620 cm^{-1}. The weak line at 410 cm^{-1} (*Figure 3a*) along with the i.r. absorption band of the same frequencies, is probably due to stretching vibrations of Mg–CH_2 in structure I[14]. The wide line of medium intensity around 960 cm^{-1} in Raman spectra of the Mg-containing polymer system (*Figure 3a*) and the medium intensive i.r. absorption bands in the same spectral range (*Figures 1a* and *1b*) can be assigned to the high-frequency mode of out-of-plane C–H vibrations in the benzene rings of structure I. In this mode all neighbouring C–H bonds vibrate out of phase[16]. This results in a noticeable distortion of the p-electron system of the benzene ring and a subsequent alteration of the electron transfer from Mg to PX_a in structure I. It also allows us to explain the difference between the poly(PX) spectrum and those of the polymer with organomagnesium structures in this frequency range; there are only very weak absorption bands around 950 cm^{-1} in the i.r. spectrum of poly(PX) (*Figure 1c*) and the lines in this range are absent at all of the Raman spectrum of the poly(PX) (*Figure 3b*).

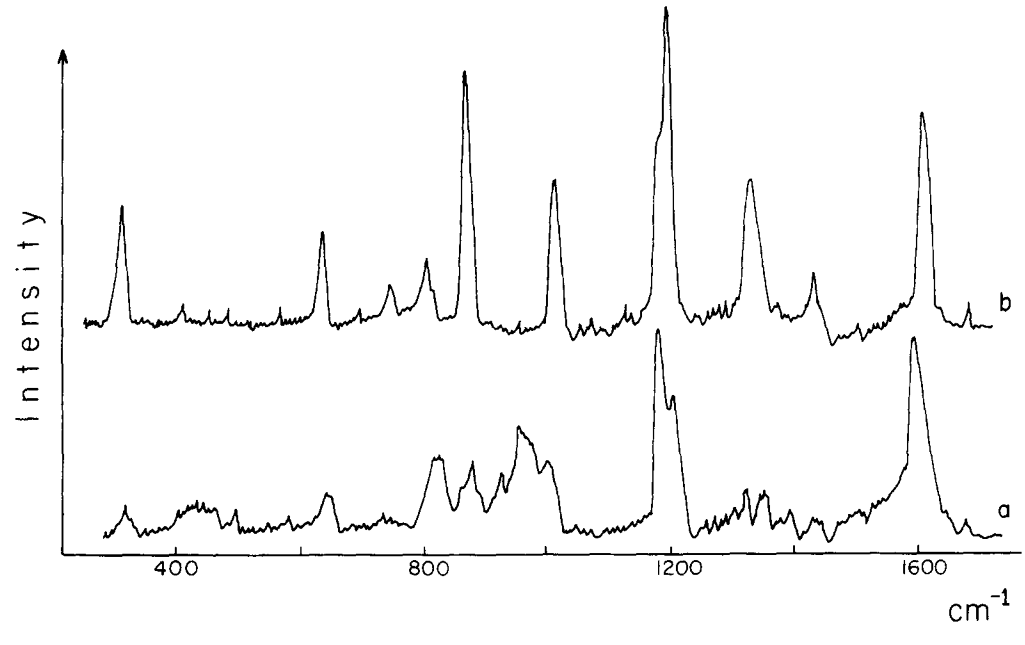
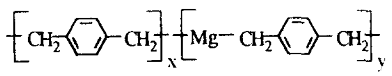


Figure 3 Raman spectra of Mg-PX co-condensate (a) and poly(PX) (b)

Further investigation is required to explain all of the spectral features obtained in the Mg-poly(PX) system. In particular, the reason for the rather low intensity of several of the lines in the Raman spectrm of organomagnesium poly(PX) is unclear. Probably, in some cases this is due to the increased ionic character of the bonds. For example, strong polarization of $MgCH_2$–benzene ring bonds in structure I gives rise to a dipole moment of the corresponding stretching vibrations (strong i.r. absorption band), but at the same time reduces the bond polarizability and intensity of the relevant Raman lines.

During photopolymerization at 80 K of the condensated Mg-PX system along with disappearance of the PX-absorption bands in the i.r. spectrum, and the appearance of the poly(PX) band at $1515\,cm^{-1}$ there is also an increase of absorption at $1500\,cm^{-1}$ demonstrated as a shoulder on the side of the $1480\,cm^{-1}$ peak (*Figure 1b*). As shown above polymerization of the Mg-PX system does not greatly affect the other i.r. absorption bands of the organomagnesium compounds. Thus we can conclude that there are two type of organomagnesium structures in the polymerized system, which are distinguished only by the influence of Mg on the benzene ring. So, structure I can be of type I_a with the ratio $Mg/PX_a = 1/1$ or of type I_b with the ratio $Mg/PX_{a=1:2}$. The electronic state and vibrations of benzene rings of these structures during the electron transfer from Mg to PX_a change much more in state I_a than in state I_b. Hence, the i.r. band at $1480\,cm^{-1}$ can be assigned to I_a and the shoulder on it around $1500\,cm^{-1}$ is attributed to I_b. It should be noted that I_a organomagnesium compounds predominate in the initial Mg-PX co-condensate with high Mg content.

According to the basic principle of organic solid state chemistry the mixture of the organomagnesium compounds and PX should form a eutectic system rather than a molecular solid solution. During the solid-state photopolymerization polymerized blocks of PX are probably coupled with blocks of I_a compound to produce block copolymer of the type



The I_b structures appear to be formed on the extremes of these blocks in the copolymer and give absorbance around $1500\,cm^{-1}$ in the i.r. spectrum.

CONCLUSION

Co-deposition of Mg-PX vapour mixture onto cooled substrate at 80 K leads to the formation of organomagnesium compounds with covalent Mg–C bonds and with a ratio of Mg to PX equal to 1. During solid-state photopolymerization these compounds are probably coupled with polymerized PX units to produce a block copolymer. On the extremes of these block structures the Mg atom is bound to two PX units.

Organomagnesium structures obtained in this way are quite stable in vacuum but are oxidatively destroyed in air at ambient temperatures.

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