

The influence of solvents on the appearance of the absorption bands of the polystyrene films deposited from solutions on metal mirrors

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Infrared reflection-absorption spectra (IRRAS) at the near-normal incidence of polystyrene films from benzene, toluene, and chloroform solutions were analyzed in this paper. The appearance of the spectrum can be affected so that false conclusions can be drawn about the positions and the shape of the absorption bands. The knowledge of these influences of residual solvents in the polymer film is important for the correct interpretation of the reflection-absorption spectra. Unlike other approaches, a single reflection at a 20° incidence angle was used. A new drop-casting technique was used for the deposition of polymer film solutions on metal mirrors. Reflection-absorption spectra at a near-normal incidence angle were obtained using a dispersive infrared spectrometer.

Keywords: IRRAS, polystyrene, transfection, residual solvent.

1. Introduction

For the study of infrared (IR) spectra of polymers, the spectra can be made in transmission when the polymer is deposited on a transparent crystal within the infrared spectral region 4000–625 cm⁻¹ [1,2].

Several external or internal reflection techniques can be used to obtain the reflection spectra of polymer films. External IR specular reflection spectra (SRS) for nontransparent polymers, IR reflection-absorption spectra (IRRAS) for very thin or micrometer thick films, or attenuated total internal reflection spectra (ATR) for very thin films may also be recorded [3–6]. For thick or opaque films, IR specular reflection spectroscopy (SRS) is used [7]. Then the Kramers–Kronig transform converts the reflection spectrum into an absorption spectrum [8–11].

Infrared reflection absorption spectroscopy (IRRAS) is one of the most common and straightforward external reflection techniques [12,13]. This technique of infrared reflection-absorption spectroscopy was first described by FRANCIS and ELLISON [14] and later developed by GREENLER [15]. Fourier transform reflection-absorption spec-

troscopy (FTIRRA), in polarized light, at the grazing incidence angle, is used for thin films with thicknesses of tens or hundreds of nanometers [16]. Infrared reflection-absorption spectroscopy (IRRAS) at near-normal incidence is used for surface films with micrometer thicknesses. The angle of incidence is typically between 0° and 45° . One or more reflections may be used. ALLARA [17] made a comparison between the single reflection mode and multiple reflections at glancing angles from a reflective metal surface. A single reflection is sufficient to record the absorption spectrum. Because the radiation passes twice through the polymer film after reflection on the metal mirror, a transfection spectrum is obtained, similar to the transmission spectrum. This technique of spectroscopy for reflection-absorption at near-normal incidence is also called transflection [18]. The spectrum obtained is dominated by transflected radiation. For this reason, the IRRA spectrum is a transmission spectrum in which the thickness of the film traversed by the radiation is twice the actual thickness of the surface film [19,20]. The absorption bands in the IRRA spectra are more intense than those recorded in the transmission for the same film because the radiation twice crosses the polymer film. Films with smaller submicrometer thicknesses can be studied in this way.

Certain precautions regarding the appearance of the spectra must be taken into account for a correct interpretation of the spectra. Changes in the appearance of the spectrum may occur due to the residual solvent, stresses inside the film, or the presence of auxiliary compounds such as additives, plasticizers, stabilizers, inhibitors, *etc.*

Polymer solutions in a suitable solvent can be used to obtain thin polymer films. After solvent evaporation, the polymer film adheres to the solid substrate, transparent (in the case of transmission or ATR spectra) or reflective (in the case of IRRA spectra).

In both spin-coated and drop-coated techniques, non-uniform film thickness can occur due to different effects [21–23]. FOWLER *et al.* [21] presented a simple experimental technique that avoids the formation of uneven films. The formation of non-uniformities in the film thickness was completely avoided by the spin-coating films at lower temperatures. The solvent may not evaporate completely and may remain in the polymer film as an impurity. In this case, the residual solvent can influence the appearance of the absorption bands of the polymer. Thus, false information can be obtained for the polymer spectrum. Solvent retention in thin polystyrene films has been studied by various methods, such as gas chromatography, neutron reflectometry, or Fourier transform infrared (FTIR) spectroscopy [24–26]. All of the methods used show that the solvent is retained at the polymer/substrate interface.

For the removal of the residual solvent, light heating and/or keeping the sample at low pressures (of the order of 10^4 Pa) are indicated. Certain precautions should be taken when heating the sample, because heating at too high temperatures can cause changes in the polymer structure [27–29].

The originality of our paper consists of the use of a new drop-casting procedure for the deposition of the polymer film solutions and the recording of reflection-absorption spectra using dispersive spectroscopy instead of Fourier transform spectroscopy. To avoid the formation of non-uniformities as a result of the evaporation of the solvent,

we used an original technique to reduce the evaporation rate of the solvent from the polymer film [19,20]. In this way, superficial films of relatively constant thickness were obtained. This method of slow solvent removal after deposition of the polymer solution was used to highlight the presence of solvent absorption bands in the 800–650 cm^{-1} region in the vicinity of the 700 cm^{-1} polystyrene absorption band. A special procedure without Fourier transformation was used for spectra collection. We used a dispersion infrared spectrometer. A simple reflection-absorption technique was used, which records the IR spectrum following a single external reflection, at a near-normal incidence angle. A comparison of reflection measurements using dispersive and Fourier transform spectrophotometers showed that both instruments are capable of measuring quality characteristics with comparable accuracy in most measured spectral regions [30,31].

2. Materials and methods

Steel, Ni, or Cu used as a substrate for the polymer film, with an area of approximately 6.7 cm^2 were obtained by polishing the surfaces to obtain good quality mirrors. Atactic polystyrene (with a molecular weight $M_w = 135 \text{ kg/mol}$ and a polydispersity index $M_w/M_n = 1.05$ from Polymer Source, Inc.) was used as received.

Polystyrene films were deposited from solutions of benzene, toluene, and chloroform. These solvents were considered the most suitable for obtaining of polystyrene solutions [32]. The deposition method used to obtain thin films was drop casting. Polymer solutions with concentrations of 0.5–4 g/L were cast by dropping them onto the horizontal surface of the metal mirrors to obtain films with different thicknesses of the order of micrometers.

The sample on which the polymer solution was deposited was covered with a Griffin beaker. The role of a beaker was to reduce the evaporation rate of the solvent to obtain superficial films of uniform thickness. Very slow evaporation of the solvent from the polymer solution in a solvent vapor-saturated environment, occurs under the spout of the Griffin beaker. In this way, superficial films of relatively constant thickness were obtained. The polystyrene film was kept under vacuum for 15 minutes at 80°C and a pressure of 12 Pa.

Some polystyrene films can be mechanically removed from the support mirror without degrading them. For these films, the transmission spectra were recorded using transparent NaCl plates. The thicknesses of the polymer films measured in transmission or reflection were obtained by measuring the interference fringes or using the RefFit fitting program [33].

Transmission and reflection-absorption spectra were recorded after two days with a conventional dispersive infrared instrument, the Carl Zeiss Jena, in the 4000–400 cm^{-1} region, at a resolution of 2 cm^{-1} . The specular reflection device of the spectrograph was used to record the IRRA spectra. Only one reflection is made on this device, which is then recorded without the Fourier transformation. The obtained spectrogram is subsequently digitized, thus obtaining the final spectrum.

3. Results and discussions

Only changes in the appearance of the infrared reflection-absorption (IRRA) spectra of the polystyrene films were investigated because of the solvent remaining in the surface film after the deposition of polymer solutions in various solvents: benzene, toluene, and chloroform. No studies have been found in the literature on the change in the IR spectra of polystyrene films due to the residual solvent.

A careful analysis of the IRRA spectra of polystyrene films deposited on metal mirrors highlights the change in the appearance of the spectrum as a result of the influence of the solvent, especially in the aromatic region. The influence of the solvent on the polystyrene spectral bands was observed both within the region 900–500 cm^{-1} of the $\text{C}_{\text{arom}}\text{-H}$ out-of-plane bending vibration and within the region 3200–2800 cm^{-1} of the stretching vibrations of both aromatic and aliphatic C-H groups. In the region of $\text{C}_{\text{arom}}\text{-H}$ out-of-plane bending vibration of the polystyrene IR spectrum, there are frequencies of out-of-plane wagging, corresponding to hydrogen atoms in the mono-substituted aromatic ring, at 757, 699, and 541 cm^{-1} [34,35]. In the region of stretching vibrations of aromatic and aliphatic C-H groups in the polystyrene IR spectrum, there are two absorption bands due to the C-H stretching vibration of the CH_2 and CH groups on the main polystyrene chain, at 2921 and 2850 cm^{-1} , respectively. The bands with peak locations at 3001, 3026, 3060, 3082, and 3105 cm^{-1} are due to the C-H stretching in the benzene ring on the polystyrene side chain [35,36].

The spectral range of 860–500 cm^{-1} of the IRRA spectra of polystyrene deposited on metal mirrors from different solvent solutions is shown in Fig. 1. The polystyrene transmission spectrum from the literature was used as a reference, in all situations [37].

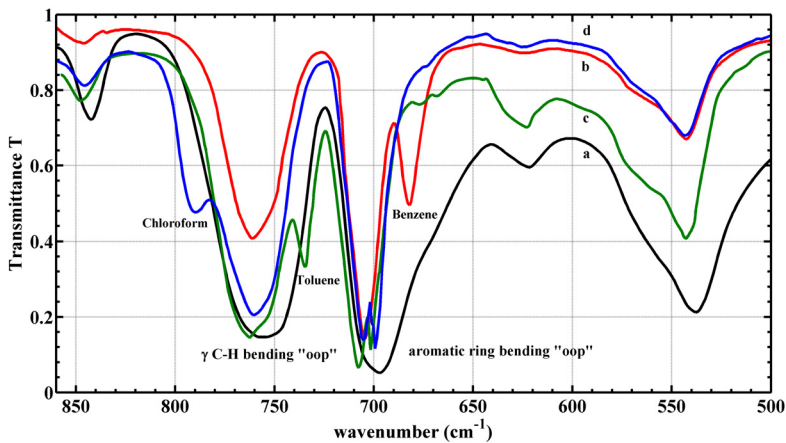


Fig. 1. The spectral range 860–500 cm^{-1} , with changes in the shape of the IRRA spectrum of the polystyrene film, due to the influence of the solvent: transmission spectrum of polystyrene (curve *a*), IRRA spectrum of the polystyrene film deposited from benzene solution (curve *b*), IRRA spectrum of the polystyrene film deposited from toluene solution (curve *c*), and IRRA spectrum of the polystyrene film deposited from chloroform solution (curve *d*).

The main change in the appearance of the reflection-absorption spectrum of the polymer film deposited from solvent solutions occurs within the region $800\text{--}600\text{ cm}^{-1}$ by the appearance of additional absorption bands due to the solvent remaining in the polymer film. Additional absorption bands as a result of the residual solvent were marked. The appearance of the spectrum within the spectral range of $860\text{--}500\text{ cm}^{-1}$ depends on the solvent used in the deposition of the polymer solution. A separate analysis of the influence of the residual solvent on the appearance of the polymer film spectrum is required for each solvent used in the deposition of the polymer film on the metal mirror.

The spectral range $3200\text{--}2800\text{ cm}^{-1}$ of the IRRA spectra of polystyrene deposited from different solvent solutions on metal mirrors is shown in Fig. 2. There is always a shift in the absorption bands of polystyrene films deposited from solutions to higher frequencies because, in this spectral region, all of the absorption bands of the solvents used are at frequencies higher than those of the polymer.

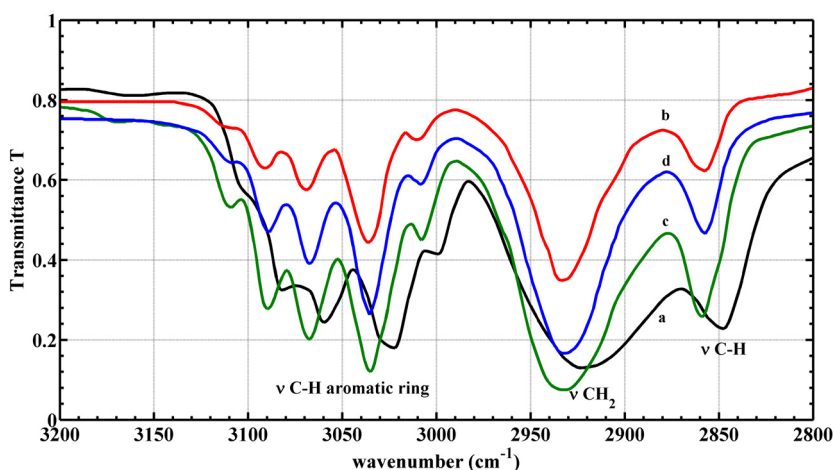


Fig. 2. The spectral range $3200\text{--}2800\text{ cm}^{-1}$, with changes in the shape of the IRRA spectrum of the polystyrene film, due to the influence of the solvent: transmission spectrum of polystyrene (curve *a*), IRRA spectrum of polystyrene film deposited from benzene solution (curve *b*), IRRA spectrum of polystyrene film deposited from toluene solution (curve *c*), and IRRA spectrum of polystyrene film deposited from chloroform solution (curve *d*).

In this paper, only changes in the $900\text{--}500\text{ cm}^{-1}$ region were analyzed because only in this spectral region significant changes in the IRRA spectra were observed due to traces of solvent remaining in the polymer films.

3.1. The influence of benzene

The spectral range $900\text{--}500\text{ cm}^{-1}$ containing absorption bands of the polystyrene transmission spectrum [37], benzene transmission spectrum [38], and absorption bands of the IRRA spectrum of polystyrene film deposited from a benzene solution on a copper

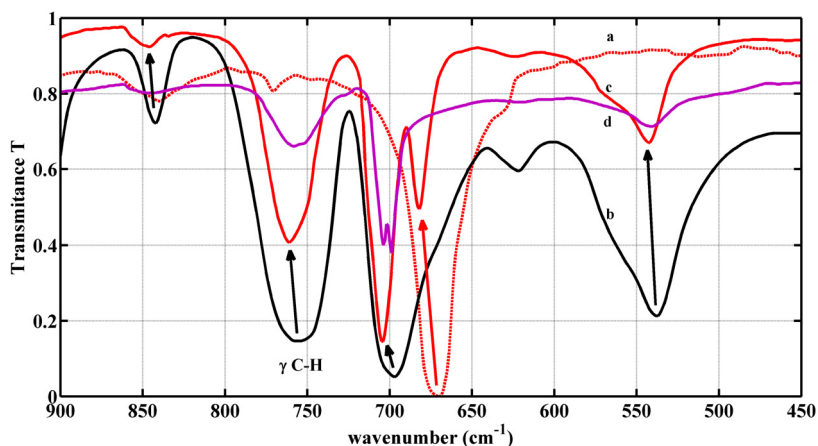


Fig. 3. The influence of the remaining benzene in the polystyrene film on the appearance of the IRRA spectrum of the polystyrene deposited on the metal mirror: transmission spectrum of benzene (curve *a*), transmission spectrum of polystyrene (curve *b*), IRRA spectrum of the polystyrene film deposited from a benzene solution (curve *c*), and transmission spectrum of the polystyrene film detached (curve *d*).

mirror is shown in Fig. 3. The IR transmission spectrum of the polystyrene film that subsequently detached from the metal surface is also shown.

More IRRA spectra of polystyrene (PS) films dissolved in benzene and then deposited on metal mirrors (copper, steel or nickel) were recorded. The PS1 and PS2 polystyrene films were deposited on steel and the PS3 and PS4 films were deposited on nickel and copper, respectively. All spectra showed an additional band at 682 cm^{-1} regardless of substrate type. The intense spectral band of benzene at 669.5 cm^{-1} induces an additional spectral band in the IRRA polystyrene spectrum due to the benzene remaining in the polymer film. The appearance of the spectrum does not depend on the nature of the substrate, but only on the thickness of the surface film and the solvent used to deposit the polymer film from the solution. The influence of the solvent was more pronounced when the superficial polystyrene film was thicker. The thicknesses of the polystyrene films were $2.2\text{ }\mu\text{m}$ for PS1, $2.5\text{ }\mu\text{m}$ for PS2, $2.3\text{ }\mu\text{m}$ for PS3^t and $1.7\text{ }\mu\text{m}$ for PS4^t. They were obtained by measuring the interference fringes or using the RefFit fitting program.

Table 1 shows the main spectral bands in the IR spectra of polystyrene [34, 37, 39] and benzene [38] (from the literature), as well as the spectral bands of the IRRA spectra of several polystyrene films deposited from benzene solutions on different metal mirrors.

Transmission (*T*) spectra of the PS3^t and PS4^t films were recorded after the films were removed from the substrates. The PS3^t film was detached from the nickel mirror (PS3) and the PS4^t film was detached from the copper mirror (PS4). For the polystyrene films detached from the metal substrates, the spectral band of 682 cm^{-1} was found to be missing due to the evaporation of the solvent. Figure 3 shows the spectral bands of PS3

Table 1. The main spectral bands within the spectral domain 1000–500 cm^{-1} of the IRRA spectra of polystyrene films deposited from benzene solutions on metal mirrors are compared with those of the polystyrene transmission spectrum.

Assignment	Intensity	Main spectral band δ [cm^{-1}]									
		Transmission spectra of polystyrene		IRRA spectra of polystyrene films (dissolved in benzene)				Transmission spectra of polystyrene detached films		Transmission spectrum of benzene	
		[34]	[37]	[39]	PS1	PS2	PS3	PS4	PS3 ^t	PS4 ^t	[38]
	Strong	538	546.9	540.5	543.2	542.4	542.7	543.2	541.1	541	–
	Weak	–	623.8	–	623.2	623.2	623.9	623.7	620.6	–	–
	Strong	–	–	–	681.4	682.8	682.1	681.4	–	–	669.5
C _{arom.} -H out-of-plane bending vibration	Strong	700	699.5	700	705.7	707.1	704.4	703.3	699.2	699.6	–
	Strong	760	756.6	756.5	761.8	763.4	761.3	761.2	758.3	755.6	771
	Weak	846	842	842	–	–	846	846.3	845.2	847	840
	Medium	907	906.8	906.5	908	–	910	903	909.1	908.6	–

and PS3^t. The PS3^t polystyrene film detached from the metal mirror was determined to have a thickness of 2.3 μm . The film thickness was obtained using the RefFit program [33].

Slight heating of the samples on which the polymer films were deposited also leads to the disappearance of the additional 682 cm^{-1} band.

3.2. The influence of toluene

The spectral range 950–600 cm^{-1} containing absorption bands of the polystyrene transmission spectrum [37], of the toluene transmission spectrum [40], and absorption bands of the IRRA spectrum of polystyrene film deposited from a toluene solution on a steel mirror is shown in Fig. 4.

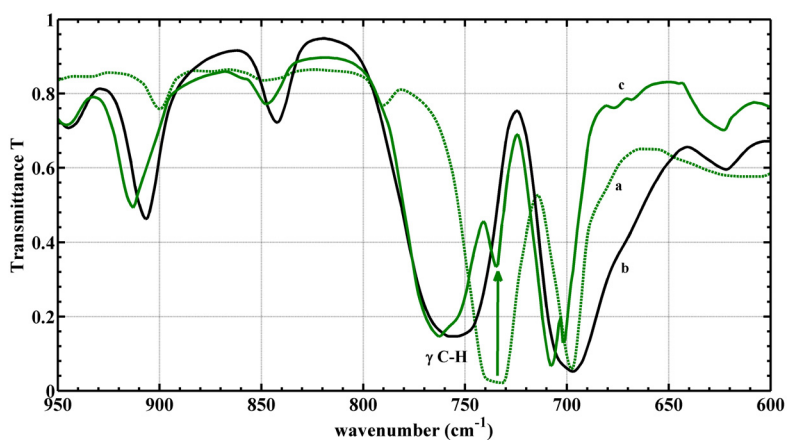


Fig. 4. The spectral range 950–600 cm^{-1} , with changes in the shape of the IRRA spectrum of the polystyrene film, due to the influence of the solvent: transmission spectrum of toluene (curve *a*), transmission spectrum of polystyrene (curve *b*), and (curve *c*) IRRA spectrum of polystyrene film deposited from toluene solution.

The intense spectral band of toluene at 731.2 cm^{-1} produces a shift in the spectral bands of polystyrene due to the toluene remaining in the polymer film. In the IRRA spectrum of the polystyrene film deposited on the metal mirror, an additional absorption band at 734.5 cm^{-1} also appears. The positions of the main spectral bands in the IR spectra of polystyrene [34, 37, 39] and toluene [40] (from the literature), as well as the spectral bands of the IRRA spectrum of the polystyrene film deposited from the toluene solution on the metal mirror, are shown in Table 2.

The intense toluene absorption band from 731.2 cm^{-1} will introduce an additional band “as a trace” at 734.5 cm^{-1} in the IRRA spectrum of polystyrene deposited from toluene solution on the metal mirror. The thickness of the PS5 polystyrene film obtained by measuring the interference fringes was 2.6 μm .

T a b l e. 2. The main spectral bands within the spectral domain 1000–500 cm^{-1} of the IRRA spectrum of the polystyrene film deposited from the toluene solution on the metal mirror, as compared to those in the transmission spectrum of toluene, and compared with those of the polystyrene transmission spectrum.

Assignment	Intensity	Main spectral band $\tilde{\nu}$ [cm^{-1}]					
		Transmission spectra of polystyrene		IRRA spectrum of polystyrene film dissolved in toluene		Transmission spectrum of toluene	
		[34]	[37]	[39]	PS5 sample	[40]	[40]
	Strong	538	546.94	540.5	542.7	–	–
	Weak	–	623.80	–	623.3	613.2	613.2
	Strong	–	–	–	701.7	–	–
	Strong	700	699.45	700	707.6	697.5	697.5
$\text{C}_{\text{arom}}\text{-H}$ out-of-plane bending vibration	Strong	–	–	–	734.5	731.2	–
	Strong	760	756.58	756.5	762.6	–	–
	Weak	–	–	–	–	–	790.3
	Weak	846	841.99	842	847.9	849.3	849.3
	Medium	907	906.78	906.5	912.7	899.9	899.9

3.3. The influence of chloroform

Figure 5 shows the spectral range of 950–450 cm^{-1} containing absorption bands from the IR transmission spectrum of polystyrene [37], the IR transmission spectrum of chloroform [41], and the absorption bands of the IRRA spectrum of polystyrene film deposited from a chloroform solution on a steel mirror.

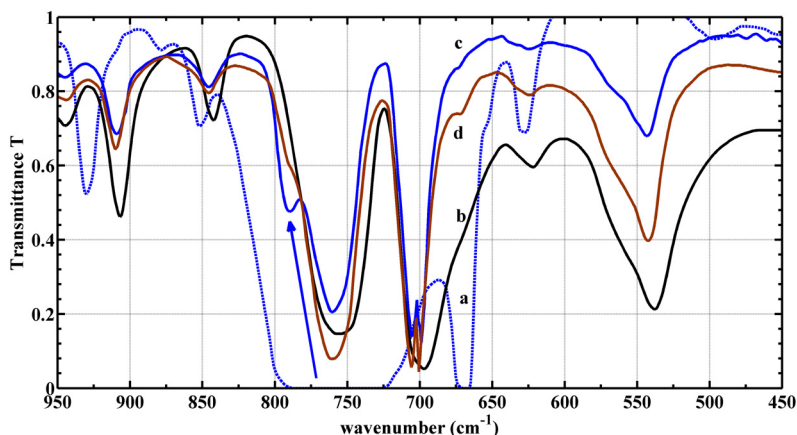


Fig. 5. Influence of the remaining chloroform in the polystyrene film on the appearance of the IRRA spectrum of the polystyrene deposited on the metal mirror: transmission spectrum of chloroform (curve *a*), transmission spectrum of polystyrene (curve *b*), IRRA spectrum of polystyrene film deposited from chloroform solution (curve *c*), and transmission spectrum of polystyrene film deposited from chloroform solution after being detached from the substrate (curve *d*).

A slight shift of all of the polystyrene IR spectral bands toward higher frequencies was observed under the influence of the chloroform IR spectral bands, located at frequencies higher than those of polystyrene. The very intense chloroform bands in the 787–726 cm^{-1} spectral region will generate an additional band at 789.5 cm^{-1} in the IRRA spectrum of the polystyrene film deposited from chloroform solution on the metal mirror.

The superficial film of polystyrene dissolved in chloroform was subsequently detached from the metal mirror. It was found that in the transmission spectrum of the polymer film detached from the metal mirror, the additional absorption band of 789.5 cm^{-1} disappears. This observation supports the assumption that the solvent used to deposit the polymer from the solution on the reflective support may persist in the polymer film and influence the appearance of the IRRA spectrum of the polymer.

The thickness of the PS^{6t} polystyrene film obtained by measuring the interference fringes of the transmission spectrum of the detached film was 2.1 μm .

The positions of the main spectral bands in the IR spectra of polystyrene [34, 37, 39] and chloroform [41] (from the literature), as well as the spectral bands of the IRRA spectrum of the polystyrene film deposited from chloroform solution on the metal mirror, are shown in Table 3.

Table 3. The main spectral bands within the 950–450 cm⁻¹ spectral domain of the IRRA spectrum of the polystyrene film deposited from chloroform solution on the metal mirror are compared with those in the transmission spectrum of chloroform, those in the transmission spectrum of polystyrene, and those in the transmission spectrum of the polystyrene film detached.

Assignment	Intensity	Main spectral band $\tilde{\nu}$ [cm ⁻¹]					
		Transmission spectra of polystyrene		IRRA spectrum of polystyrene film dissolved in chloroform	Transmission spectrum of detached film	Transmission spectrum of chloroform	
		[34]	[37]	[39]	PS6 sample	PS6 ^t	[41]
	Strong	538	546.94	540.5	543.2	542.5	496
	Weak	–	623.80	–	623.7	624.2	626.4
	Strong	–	–	–	699.4	700.6	665–670
	Strong	700	699.45	700	705.3	705.8	
	Strong	760	756.58	756.5	760.7	762.2	726–787
	Strong	–	–	–	789.5	–	
	Weak	846	841.99	842	845.5	845.4	852.3
	Medium	907	906.78	906.5	909.5	910.3	930.5

4. Conclusions

The originality of this paper consists in the use of a new drop-casting procedure for the deposition of the polymer film solutions and the recording of reflection-absorption spectra using dispersive spectroscopy instead of Fourier transform spectroscopy. The technique of deposition of the polymer solution used allows a better highlighting of the presence of the remaining solvent in the film. A much simpler reflection-absorption technique (called transflection) was used, which records the IR spectrum following a single external reflection at small angles of incidence. The results obtained and presented by us show that the IRRA technique can be used as a very good method for studying the residual solvent in the polymer film because the appearance of the IR spectrum is very sensitive to changes in the structure of the polymer.

In the case of polymer films deposited from solutions of various solvents, traces of solvent may remain in the polymer mass after evaporation and influence the appearance of the IR spectrum.

In the IRRA spectrum of polystyrene, additional absorption bands were observed at frequencies: 682 cm^{-1} for polystyrene dissolved in benzene, 734.5 cm^{-1} for polystyrene dissolved in toluene, and 789.5 cm^{-1} for polystyrene dissolved in chloroform. In the spectral region $2800\text{--}3200\text{ cm}^{-1}$, only displacements of the absorption bands were observed in the IRRA spectra of the polystyrene films deposited from solutions toward higher frequencies due to the influence of the intense bands of the solvents used. This paper warns about false information that can be obtained from these modified spectra. Changes in the appearance of the spectrum due to the residual solvent must be taken into account when interpreting the IRRA spectra of the polymer.

Light heating of the polymer cast on the metal mirror for 15 minutes is insufficient to remove the residual solvents in the film. In this paper, we report that even after the samples were kept for a few days in the ambient atmosphere, the presence of the remaining solvents in the polymeric films was found. To remove the remaining solvent in the polymer film, it is necessary to gently heat the sample or keep it in a light vacuum atmosphere, without degradation of the polymer. Certain precautions should be taken when the sample is heated because heating at too high temperatures can cause changes in the polymer structure.

The IR transmission spectrum of the detached film was recorded when the polystyrene film could be detached from the metal mirror. Additional bands were not detected in the IR transmission spectrum of the polystyrene film because the solvent remaining in the film was evaporated after the film was peeling off the substrate.

We observed that the appearance of the IRRA spectrum of the polystyrene film deposited from solutions on metal mirrors can depend on the solvent used to deposit the polymer film in the solution, the thickness of the surface film, and it does not depend on the nature of the substrate. The influence of the solvent was more pronounced when the superficial polystyrene film was thicker.

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