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The anisotropy of poly(acrylic acid) in composites with liquid crystalline cellulose derivatives as seen by low-frequency Raman spectroscopy

Marcin Kozanecki[a], Eugene Duval[b], Jacek Ulanski[a,*], Lidia Okrasa[a], Lucien Saviot[b]

[a]Department of Molecular Physics, Technical University of Lodz, 116 Zeromskiego St., 90–924 Lodz, Poland
[b]Laboratoire de Physico-Chimie des Materiaux Luminescents, Universite Claude Bernard - Lyon-1, 43 Bd. du 11 Novembre, 69622 Villeurbanne Cedex, France

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Abstract

The low-frequency Raman scattering (LFRS) was used in order to determine the orientation of poly(acrylic acid) in anisotropy composite with liquid crystalline [(propionyloxy)propyl]cellulose (PPC). The photopolymerisation of acrylic acid in the presence of PPC leads to the formation of the poly(acrylic acid) (pAA) anisotropic network. This anisotropy is stable even at temperatures higher than the temperature of the optical isotropisation of the PPC/pAA composite. The comparison of the LFRS and thermooptical data proves the hypothesis explaining of the reversibility of the optical birefringence in the PPC/pAA composites by formation, in a course of photopolymerisation of anisotropic pAA network. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Composite; Poly(acrylic acid); Low-frequency Raman scattering

1. Introduction

An anisotropic systems with liquid crystalline (LC) organisation of cellulose derivatives (CD) macromolecules have been known for many years [1-3]. They can be readily oriented mechanically, which results in materials with interesting optical properties. Unfortunately, the thermal stability of the orientation of such solutions is poor. After the cessation of shearing the metastable band texture is observed through a polarising microscope as an effect of non-complete stress relaxation. However, further stress relaxation leads to the thermally stable polydomain chiral-nematic mesophase called grain texture [3-8]. In order to freeze the orientation of macromolecules one proposed to use the solvents capable of photopolymerisation, e.g. *N,N*–dimethylacrylamide [9], 2–hydroxyethyl methacrylate [10], methacrylic acid [11], and acrylic acid (AA), which was used in this study [12-14]. As a result of the photopolymerisation of such solvents, being also vinyl monomers, in mechanically oriented lyotropic LC solutions of CD one obtained the composites with a stable band texture. The thermooptical analysis (TOA) shows, that the birefringence of such systems is thermally stable and reversible, which means that during the cooling of the sample (which was previously heated to a temperature higher than its temperature of isotropisation), the previous birefringence appears. This suggests that the network of poly(acrylic acid) (PAA) macromolecules (formed in a medium of oriented LCCD) is oriented, and that its topological anisotropy induces the orientation of the CD macromolecules during cooling from the isotropic state [4,5,11-14].

The low-frequency range (1–100 cm^{-1}) of Raman scattering (LFRS) provides information about the supramolecular structure and the structural relaxation in amorphous materials. Generally, the LFRS of glasses consists of two components. The first one is due to the harmonic (or vibrational) motions and is called the boson peak. The harmonic low-frequency modes are extended on nanometric lengths, and they are transversal or torsional. The second part is an effect of anharmonic (or relaxation) motions, and is called quasielastic light scattering [15]. The Stokes LFRS intensity $I(\omega)$ is given by [18]:

$$I(\omega) = C(\omega)g(\omega)[n(\omega, T) + 1]/\omega \qquad (1)$$

where: ω is the wavenumber, $C(\omega)$ is the light-vibrational coupling coefficient, $g(\omega)$ is the density of vibrational states, and $n(\omega)$ is the Bose factor. The “excess” of the $g(\omega)$ observed by Raman scattering at the low-frequency range (boson peak) [15,18], as well as by inelastic neutron scattering [19,20] has been correlated with an anomaly characteristic of specific heat and thermal conductivity [16,17]

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* Corresponding author. Tel.: +48-42-631-3216; fax: +48-42-636-8522.
E-mail address: julanski@ck-sg.p.lodz.pl (J. Ulanski)

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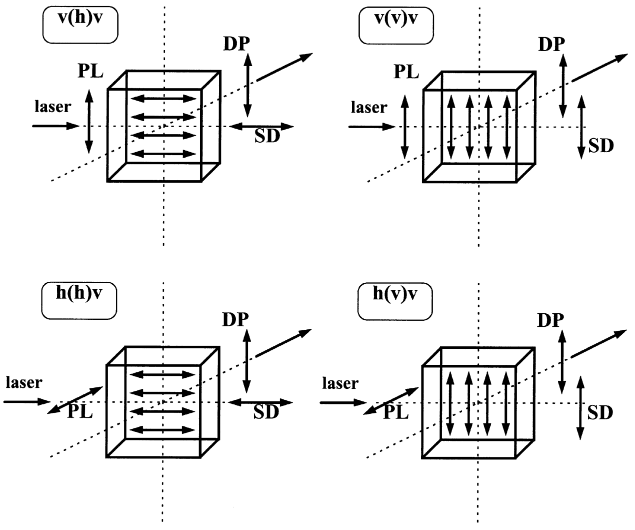

Fig. 1. Set-up configuration used for Raman investigation of the PPC/pAA composite. PL: polarisation plane of the laser light, SD: shear direction of composite, DP: polarisation plane “detected” by apparatus.

found for glasses. For amorphous polymers, Duval et al. [21] have proposed to explain these anomalies by their non-continuous structure. They suggested that the entangled structure of the polymer melt persists after freezing.

In this paper we focus our interests on the determination of the orientation of pAA in anisotropy composite with [(propionyloxy)propyl]cellulose (PPC), which is a LCCD. This was investigated by LFRS. Earlier investigations of LFRS have shown that it is very useful in the study of oriented amorphous polymers [22,23] and partially crystalline polymers [24]. But to the best of our knowledge, this is the first time that LFRS was used to investigate the composites.

2. Experimental

The [(priopionyloxy)propyl]cellulose was obtained from (2–hydroxypropyl) cellulose (Aldrich Chemical Co., M.W. = 100000), as described in literature [2]. The films of pAA were obtained by radical photopolymerisation of pure AA using the Erasure 651 (Ciba–Geigy) as a photoinitiator, and a UV-lamp (365 nm) as a light source. The PPC/pAA composites 40:60 (% w/w) were obtained by photopolymerisation of mechanically oriented thin films (c.a. 180 μm) made of the appropriate LC solutions of PPC in acrylic acid under the same conditions as pure pAA. A detailed description of the preparation of the composites is given elsewhere [4,5,11–14].

The Raman spectra were obtained using the quintuple monochromator Z–40 DILOR equipped with a photon counting system. The 647.1 nm line of the Kr laser was chosen to excite the samples in order to avoid the fluorescence. The power of the laser light was about 200 mW. The high temperature investigation was made using the hot stage with a temperature stabilisation of ±1 K. The spectra were obtained after the stabilisation of the samples in each temperature for 30 minutes. Four configurations of the oriented sample and of the polarisation of the laser were used, as presented in Fig. 1. The monochromator transmits the vertically polarised light. In order to normalise all the spectra, we divided the $I(\omega)$ values by $\omega[n(\omega) + 1]$.

The TOA was performed using a polarising microscope

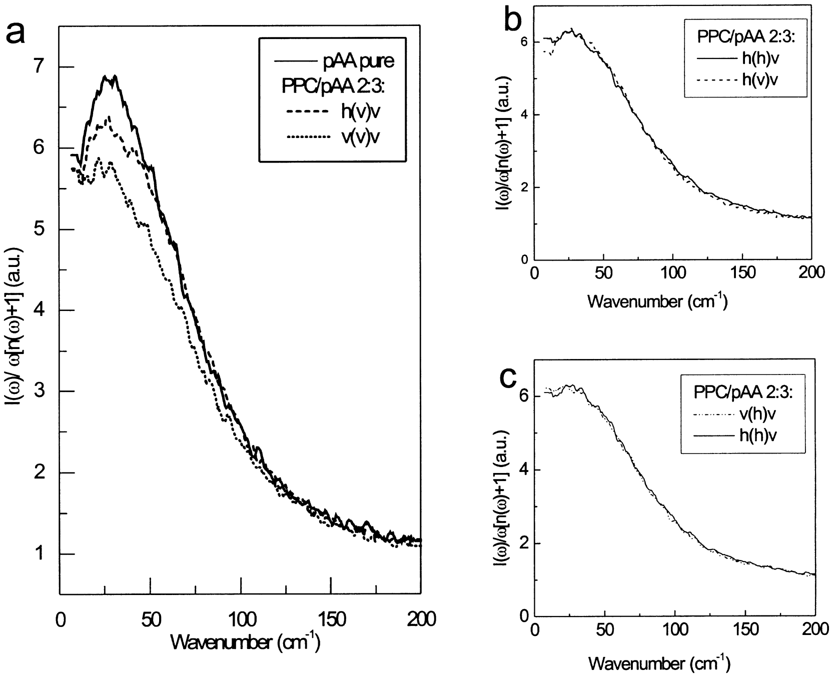

Fig. 2. Comparison of the room temperature LFRS of the pure pAA and PPC/pAA composite obtained at different configurations.

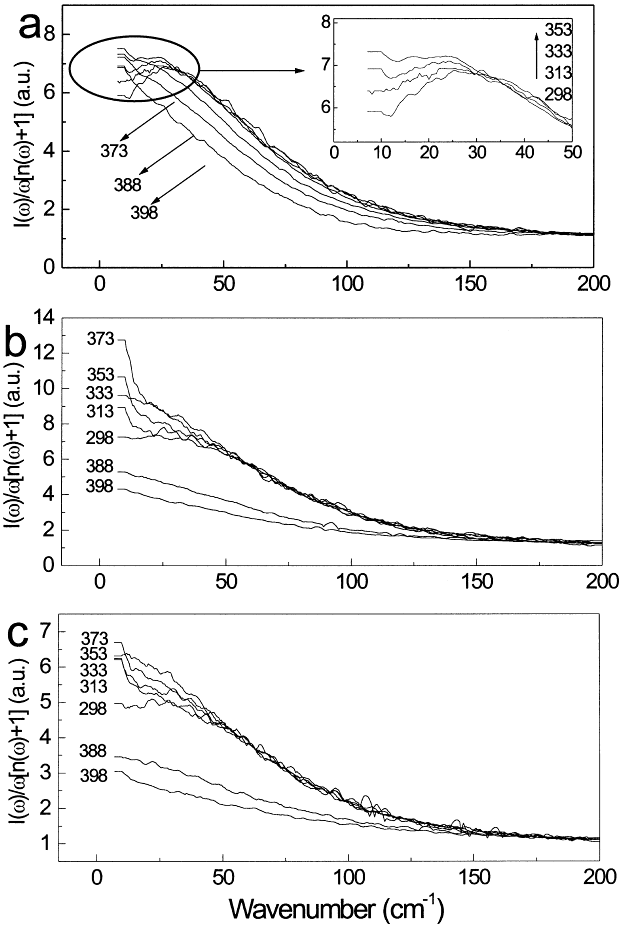

Fig. 3. Temperature dependence of the $I(\omega)/\omega[n(\omega)+1]$ for pure pAA (a) and the PPC/pAA system at v(h)v (b) and v(v)v (c) configurations of set-up.

equipped with a Mettler FP–82 measuring cell. The changes of optical anisotropy were determinated by monitoring the transmission of polarised light θ/θ_0 (where θ_0 is the transmission at room temperature) of the sample oriented diagonally between crossed polarisers.

3. Results

The room temperature LFRS of the PPC/pAA composite at h(v)v and v(v)v configurations are shown in Fig. 2a. The spectrum of pure pAA is presented in the same figure. The spectra of the composite at h(h)v and v(h)v configurations, compared with the spectrum at the h(v)v configuration, are presented in Figs. 2b and 2c, respectively. They are practically identical. It is remarked that in all of these cases the polarisation of the laser light is perpendicular to the direction of the orientation of macromolecules in the composite. Fig. 2c shows additionally that the polarised and depolarised spectra of the composite are identical.

For pure pAA, a maximum corresponding to the so-called boson peak exists at about 26 cm^{-1}. The presence of PPC during the photopolymerisation of AA induced a decrease of the boson peak; this was observed for all the configurations. The maximum of the boson peak for the composite appears at 26 cm^{-1} just as that of pure pAA (except for the v(v)v configuration), but in addition, a shoulder at higher frequency (50 cm^{-1}) can be observed. This shoulder is due to the presence of PPC as one can deduced from the spectra of pure PPC. The small shift of the boson peak to a lower frequency (to 24 cm^{-1}) with respect to the spectrum of pure pAA is visible in the spectrum of the composite only when the polarisation plane of the laser light is parallel to the direction of shearing; in another words, at v(v)v configuration. In this case the Raman intensity of the boson peak is lower than for the other configurations.

The temperature dependence of the LFRS of pure pAA and of the PPC/pAA system are presented in Figs. 3a,b,c. The increase of the temperature to 353 K induces a small increase in the Raman intensity at a very low frequency for pure pAA (see Fig. 3a). This is probably due to the increasing contribution of quasielastic scattering to the *I(ω)*. The new tendency appears close to the T_g of pAA (about 378 K). The intensity of the boson peak starts to decrease with the increasing of the temperature. Similar effects are visible in the composite for both v(h)v and v(v)v set-up configurations, except that the highest intensity appears not at 353 K, but at 373 K.

At the higher temperatures used, just as at room temperature, the spectra for the composite are different only for v(v)v configuration, while for other configurations they are the same. *I(ω)* at wavenumbers below 100 cm^{-1} for the composite is also lower compared to the spectrum of pure pAA.

4. Discussion

The most pronounced change in the Raman spectra presented in Fig. 2 (induced by the presence of PPC in the process of photopolymerisation) is the decrease of the boson peak for the composite as compared to the spectrum of pure pAA. It is not very surprising and can be explained by the effect of the dilution of pAA. More interesting is the comparison of the spectra of the PPC/pAA composite obtained at different set-up configurations. Two major differences appear between the spectrum for the v(v)v configuration and the spectra for other configurations. The first one is the lower intensity of the boson peak when the polarisation of the laser beam and of the scattered light are parallel to the shear direction (v(v)v configuration). This is with agreement with previous experiments on oriented poly(methyl methacrylate): it was observed that the low-frequency Raman scattering is more intense when both polarisation (laser and scattered light) are perpendicular to the orientation (v(h)v) [23]. The second is the small shift of the maximum of *I(ω)* observed in this configuration. These differences prove that the pAA macromolecules in the composite are oriented. It is interesting to note that a similar

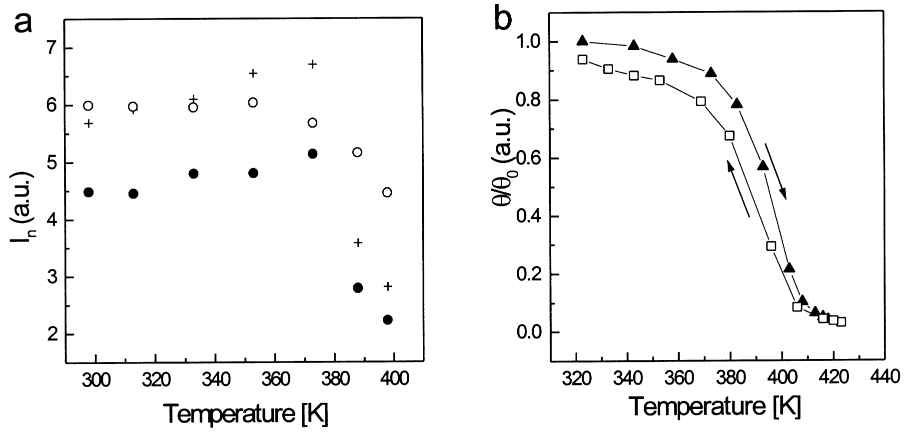

Fig. 4. a: Temperature dependence of the $I_n(\omega)$ for pure pAA (crosses) and for the PPC/pAA system at v(h)v (open circles) and v(v)v (full circles) configurations; b: relative light transmission θ/θ_0 under crossed polarisers for the PPC/pAA system: during heating (full triangles) and cooling (open squares).

dependence of the intensity of the spectra of the composite at different set-up configurations has been observed at higher temperatures (compare with Fig. 3). The TOA has shown that the temperature of isotropisation of the PPC/pAA system is about 405 K (see Fig. 4b). Unfortunately, it was impossible to investigate the composite by LFRS at temperatures above 398 K because of the fluorescence induced by heating. This is probably due to the ionic impurities which residue after the preparation of PPC, or possibly the dissociation of pAA. Dielectric investigations have shown a very strong increase of ionic conductivity at elevated temperatures [14]. But even at 398 K, after about 20 minutes of annealing, the composite is practically optically isotropic. The position of the maximum of *I(ω)* is invisible at 398 K in all the investigated materials (see Fig. 3) because of the increasing contribution of the quasielastic scattering to the *I(ω)*. This is due to the increasing contribution of anharmonic modes, and to a decrease of the intensity of the boson peak. Because of this, an analysis of the boson peak position is impossible, and we have focused our interest only on studies of temperature dependence of the *I(ω)* for pure pAA and for the PPC/pAA system for parallel (v(v)v) and perpendicular (v(h)v) configurations of the polarisation plane of the laser light and shear direction of the composite (see Fig. 3).

We calculated the ratio $I_n = I(30)/I(200)$ in order to normalise the intensity of all the spectra. The temperature dependencies of I_n for v(v)v and v(h)v configurations of the composite and of pure pAA are plotted in Fig. 4a. The decrease of the I_n value corresponds to the T_g of pAA. For the oriented composites, these dependencies correlate very well with thermooptical analysis data in all cases. The decreasing of the θ/θ_0 value (this being the measure of the optical anisotropy) starts at about 373 K, which is the same temperature characteristic of the start of the decrease of I_n. This temperature is very close to the T_g of pAA found by us by the DSC investigation in the range from 378 K for pure pAA to 381 K for pAA in composite with PPC. This coincidence can be explained assuming that pAA forms the anisotropic network. Above the T_g of pAA, the mobility of the segments of pAA macromolecules increases so that the macromolecules of PPC can move. This leads to the disappearance of the optical anisotropy. The increase of the mobility of the pAA segments also leads to the increase of the quasielastic contribution (effect of anharmonic motions) to the scattered light spectra at the cost of the intensity of the boson peak (effect of harmonic vibrations). The anisotropy of the Raman spectra of the composite at v(v)v and v(h)v configurations at 398 K suggests that the pAA chains are anisotropically oriented (probably a nanoscopic scale) even if the optical anisotropy decays. This is in an agreement with our earlier model of the anisotropy pAA network proposed for the explanation of the reversibility of the optical anisotropy in composites. Such an effect [4,5,11-14] is presented in Fig. 4b.

As a measure of the anisotropy (A_n) of pAA, we

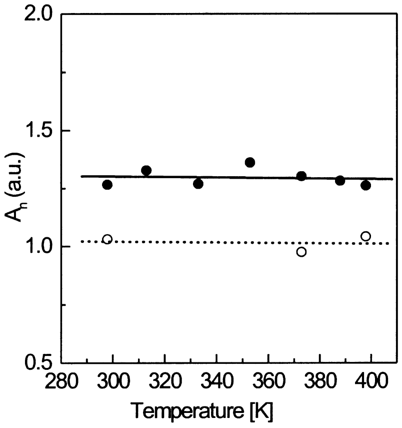

Fig. 5. Temperature dependence of the A_n of the PPC/pAA composite (full circles) and for pure pAA (open circles).

calculated the A_n value defined as follows:

$$A_n = I_n^{\mathrm{v(h)v}} / I_n^{\mathrm{v(v)v}} \tag{2}$$

where $I_n{}^{\mathrm{v(h)v}}$ and $I_n{}^{\mathrm{v(v)v}}$ are I_n for the v(h)v and the v(v)v configurations, respectively. For pure pAA, the A_n equals 1 and is independent on the temperature, which is characteristic for isotropic materials. Fig. 5 presents the temperature dependence of the A_n. In the investigated range of temperatures, the A_n is constant and equal to about 1.26 for the composite. It proves that the anisotropy of pAA is stable, even at higher temperatures, and that the pAA network could be the matrix for the orientation of PPC macromolecules during cooling of the composite previously heated to a temperature higher than the temperature of its optical isotropisation.

5. Conclusion

The low-frequency Raman spectroscopy investigations show that the photopolymerisation of AA in the presence of LCCD such as PPC leads to the formation of the pAA anisotropic network. The anisotropy of this network is stable even at temperatures higher than the temperature of the optical isotropisation of the PPC/pAA composite. The comparison of the LFRS and TOA data proves the possibility of the explanation of the reversibility of the optical birefringence by the model of the anisotropic pAA network penetrating the PPC phase.

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