



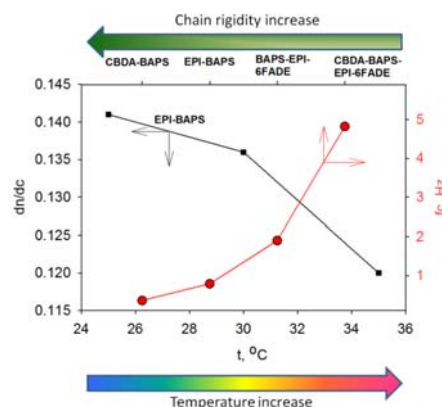
POLYIMIDES CONTAINING CHALCOGEN ATOMS IN SOLUTION PHASE: VISCOELASTICITY AND INTERFEROMETRY ANALYSES

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Solutions of four aromatic/alicyclic polyimides containing chalcogen atoms were prepared and characterized by means of rheology and interferometry studies. The distinct flexibility of the PI samples is reflected on the optical and rheological properties. This aspect could be more evidenced when the experimental temperature is ranged. The polyimides containing flexible segments and angular bonds along the main chain reveal a higher impact of temperature on the specific refractive index increment. This was further correlated with shear oscillatory tests, which indicated that the relaxation time is reflecting the backbone flexibility and is decreasing at higher temperatures. The obtained results are important in understanding solution properties of polymers that are to be processed into shielding layers for photovoltaic devices.



INTRODUCTION

Thermostable polymers, like polyimides (PIs), have found utility in numerous technical areas, including inter-layer dielectrics,¹ light-emitting diodes,² components for transistors,³ alignment layers⁴ and shielding materials for photovoltaic devices.⁵ For the latter application, the material must have elevated optical transparency, high refractive index, and thermooxidative stability. These features are typical for PIs containing aliphatic units and chalcogen atoms.^{5,6} The resulting film properties are dependent not only on the polymer chemical structure, but also on the processing conditions.⁷ For this reason, the PI characteristics in solution phase must be closely investigated to ensure optimal processability of the final product.

During compounding, there are many factors that affect the morphology through the shear response of polymer, solvent nature or specific interactions occurring in the system. Rheology is a versatile tool that explains the sample's response to deformation and it is largely employed to evaluate material's reliability.⁸ The solution viscoelastic character is an important parameter that influences the quality of the polymer films. Moreover, polymer concentration in solution determines the variation of optical properties, such as specific refractive index increment (dn/dc). This parameter is impacted by chemical identity of the used solvent to formulate the solution, the temperature at which the measurements are conducted, and the light wavelength. The dn/dc is also relevant for estimation of the dimensions, shapes, and molecular weights of polymers.⁹ Therefore, there is

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a relation between the viscoelastic properties and dn/dc if considering the fact that chain flexibility will determine a particular spatial conformation that is reflected in a corresponding relaxation time upon cessation of the shear deformation. Such aspects could provide novel insights on understanding PI solution behavior and therefore processing in optimal conditions to obtain stable and uniform films for photovoltaics.

This article describes original data on shear oscillatory properties of some PIs containing aliphatic units derived from alicyclic dianhydride (1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA), 5-(2,5-dioxotetrahydro-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (EPI)), and aromatic segments derived from diamines containing chalcogen atoms (bis[4-(4-amino-phenoxy) phenyl] sulfone (BAPS) and 4,4'-(hexafluoroisopropylidene)bis(p-phenylene-oxy)dianiline (6FADE)). The data were also correlated with those extracted from specific refractive index increment measurements to acquire information on PI solution processing. The temperature was ranged in order to study its impact on the pursued properties of PIs in solution phase. These results are relevant for obtaining thermostable polymer layers for photovoltaics shielding.

RESULTS AND DISCUSSION

Interferometry analyses are made on N,N-dimethylacetamide (DMAc) solutions of the four selected PIs containing chalcogen atoms (O and S). Theoretical assessment of the specific refractive index increment (dn/dc_{theor}) is possible through the relation developed by Huglin,¹⁰ shown in equation (1):

$$\frac{dn}{dc} = \vartheta_p \left(\frac{n_p^2 - 1}{n_p^2 + 2} - \frac{n_s^2 - 1}{n_s^2 + 2} \right) \frac{(n_s^2 + 2)^2}{6n_s} \quad (1)$$

where ϑ_p is the partial specific volume of polymer in solution, while n_p and n_s are the refractive index of the polymer and solvent, respectively.

As seen in Huglin relation (1), for evaluation of dn/dc , it was necessary to measure the refractive index of polymer solution and that of the solvent. The refractive indices of the PI solutions can be viewed as additive functions of the solvent and polymer compositions, as presented in relation (2):

$$n_{sol} = w_s n_s + w_p n_p \quad (2)$$

where w_s and w_p are the weight fractions of solvent and polymer in the system.

Using the measured refractive properties of the PI solutions and based on equation (2), it was possible to calculate the refractive index of the polymer samples and further use the data for estimation of dn/dc_{theor} . The specific refraction index increment values of each solved PI, determined by refractometry and calculated with equation (1), are listed in Table 1. The molar volume was calculated based on group contribution theory and the corresponding structural increments were taken from literature.^{11,12}

The differences recorded between the theoretical and the experimental values are very small and they might be caused by a slight absorption, which affected the achieved data. It can be seen that the increase of temperature leads to a slight reduction of the dn/dc values. The PI samples containing flexible EPI sequences and kinks ($>SO_2$ or $>C(CF_3)_2$) in the main chain present a higher impact of temperature on the magnitude of the specific refractive index increment.

Small amplitude oscillatory shear experiments were made to measure the stress response of the PI solutions and understand its correlation with the chemical structure. In the linear viscoelastic (LVE) domain, the application of very small stresses leaves undisturbed the macromolecular structure and as a result no relevant modifications in the elastic modulus G' are remarked (see Figure 1).

Table 1

The values of the molecular weight of the structural unit (m_{us}), molar volume (V_{us}), specific volume (v_p), refractive index of polymer solution (n_{sol}), theoretical specific refractive index increment (dn/dc_{theor}) and experimental specific refractive index increment (dn/dc_{exp})

Solution sample	m_{us}	V_{us}	v_p	n_{sol}			dn/dc_{theor}			dn/dc_{exp}
				25°C	30°C	35°C	25°C	30°C	35°C	25°C
EPI-BAPS	660	452.75	0.686	1.5164	1.5022	1.4979	0.141	0.136	0.120	0.143
CBDA-BAPS	592	390.97	0.660	1.5245	1.5101	1.5063	0.154	0.146	0.133	0.155
BAPS-EPI-6FADE	1146	811.90	0.708	1.5044	1.4876	1.4852	0.126	0.117	0.102	0.128
CBDA-BAPS-EPI-6FADE	1338	893.35	0.668	1.4963	1.4771	1.4744	0.105	0.092	0.077	0.106

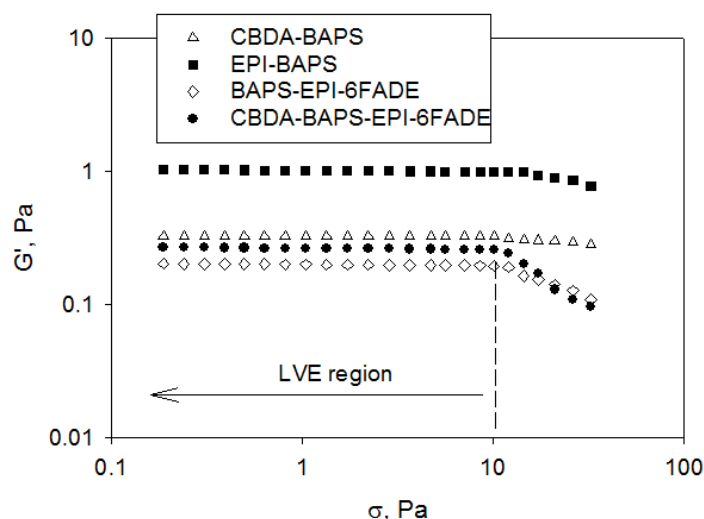


Fig. 1 – Shear storage modulus against shear stress for the PI solutions at 25°C at frequency of 1 Hz.

At a critical stress, the storage modulus G' tends to decrease because the structure is gradually disturbed. After this point, the end of the LVE zone is attained: here the plateau value of G' can be linked to the rigidity of the sample at rest. For the prepared PI solutions, the deviation from linear behavior is noted at a critical stress of ~ 1 Pa. Given the latter observation, this value was further used for frequency sweep tests, which are depicted in Figure 2. When applying small shear frequencies, the PI solutions start to behave as a “liquid-like” material, where the prevalent component being the viscous one ($G' < G''$). Thus, the zone of small frequencies from Figure 2 is depicted by a power law of the rheological moduli, namely: $G' \sim f^2$ and $G'' \sim f^1$, as generally remarked for viscous fluids.¹³ Subsequent frequency augmentation leads to a progressive increase of the elastic component G' in detriment of the viscous one G'' . Such increase in frequency continues up to a point where $G'=G''$ and then $G' > G''$ (“solid-like” character of the PI solutions). The samples undergo a transition from viscous to elastic flow and the frequency attributed to the point of shear moduli crossover is denoted f_c . The values of the f_c are paramount for discussing the relaxation properties of the investigated PI solutions. According to Figure 2, one may notice that the different chain flexibility of the samples determines distinct changes in the global PI structure as a result of the imposed shear intensity. During the applied deformation, variations in the speed and the flow time generate different amounts of anisotropy in each sample. The reversion to

quiescent state demands the relaxation of the PI chains in DMAc to the initial state of isotropy through the action of Brownian motion and internal springs connecting the chain segments. As a conclusion, for the examined PI solutions, the f_c and relaxation time are affected by main chain flexibility. The achieved data at 25°C reveal that the crossover frequency ranges as follows: CBDA-BAPS $<$ EPI-BAPS $<$ BAPS-EPI-6FADE $<$ CBDA-BAPS-EPI-6FADE. This is in agreement with PI chemical structure, namely: the small and rigid CBDA moieties lead to a stiffer PI backbone comparatively to the polymer structures containing non-symmetric and bulky EPI units which have a supplementary single bond, providing an additional freedom degree. Moreover, regarding the structure of the used diamines, one may notice that the presence in their corresponding segments of ether bonds between aromatic phenyls, combined either with $>SO_2$ or $>C(CF_3)_2$ bridges, generates additional torsion points of the PI chains, increasing the overall flexibility. In addition, literature¹⁴ shows that $>C(CF_3)_2$ group is considered more flexible comparatively with $>SO_2$ one.

Very important, the variation order of the f_c parameter for each studied PI solution can be well correlated with dn/dc data that are decreasing for higher chain flexibility. Kim *et al.*¹⁵ reported that dn/dc is influencing the radius of gyration and hence the conformation of polymer chains in solution. According to their study, a higher value of dn/dc is linked to a bigger R_g parameter and denotes a more rigid chain. Therefore, the dn/dc and shear oscillatory results confirm the flexibility of the analyzed PI samples.

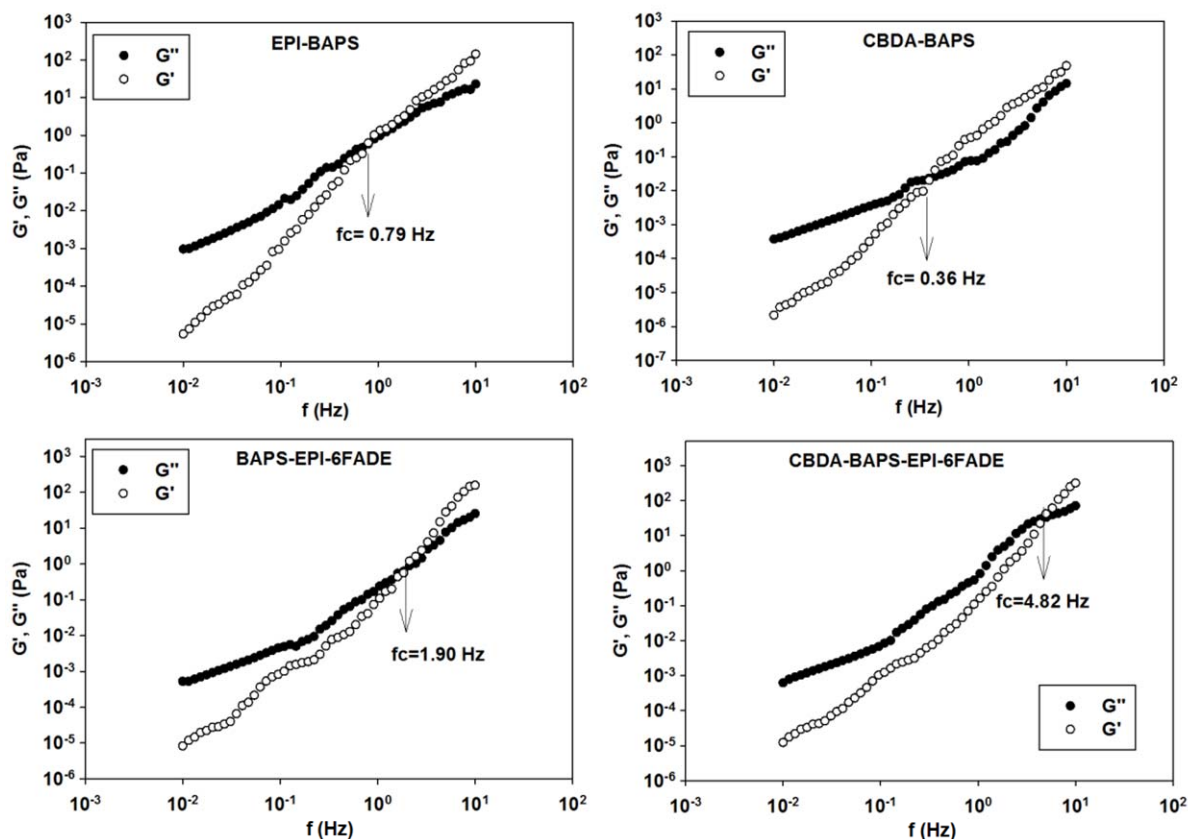


Fig. 2 – Shear oscillatory tests of the PI solutions at 25°C.

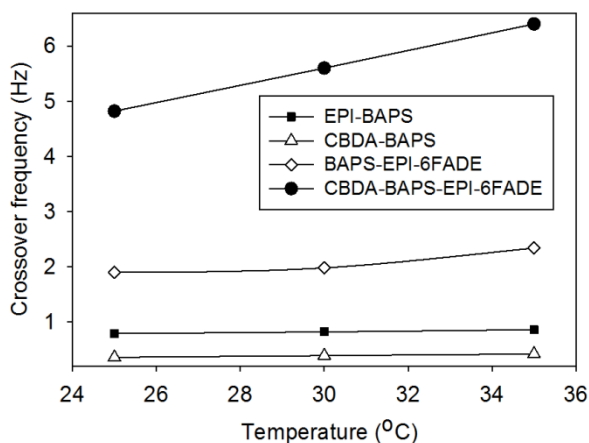
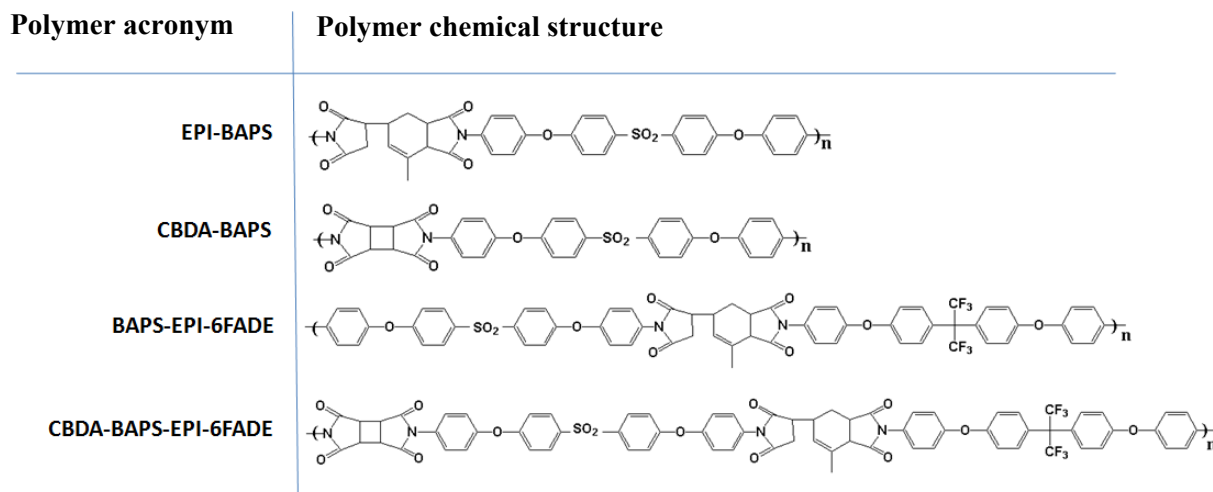


Fig. 3 – Crossover frequency variation with temperature for the PI solutions.

Figure 3 indicates that the increase in temperature generates an increase in the crossover frequency value. This means that the temperature is a positive factor that upon rising determines more facile movement chain segments in solvent medium and renders better flexibility, hence induces quicker relaxation and higher f_c values. According to Figure 3, the larger flexibility of the PIs that contain EPI, BAPS and 6FADE segments determines a faster increase of the f_c values, so

these samples are recovering easier after shear cessation. Such solution behavior enables a facile processing into resistant and dimensionally stable polymer layers for many applications. The study of the conditions where the sample response to shear results in deformations, which enable the sample recovery and lead to dimensionally stable and flexible films, opens perspectives in processing shielding polymer layers for photovoltaics technologies.



Scheme 1 – The chemical structures of the studied imidic polyimers.

EXPERIMENTAL

The monomers used in synthesis are: 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA, TCI Chemicals), 5-(2,5-dioxotetrahydro-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride) (EPI, Merk), bis[4-(4-aminophenoxy) phenyl] sulfone (BAPS, TCI Chemicals) and 4,4'-(hexafluoroisopropylidene)bis(p-phenyleneoxy)dianiline (6FADE, TCI Chemicals). The polyimides were obtained by polycondensation method, which is previously described in literature⁶. The structures of the analyzed imidic polymers are illustrated in Scheme 1.

Polymer powder (concentration ~ 3%) is solved in N,N-dimethylacetamide (DMAc) and stirred to result homogeneous solutions that are further studied.

The number average molecular weights, M_n , of the samples were achieved by gel permeation chromatography measurements in N,N-dimethylformamide (DMF) on a PL EMD-950 device. The M_n is 29 000 Da for EPI-BAPS, 34 000 Da for CBDA-BAPS, 43 000 Da for BAPS-EPI-6FADE and 47 000 Da for CBDA-BAPS-EPI-6FADE.

Viscoelasticity tests of the PI solutions were made on a Bohlin CS50 device from Malvern Instruments at 25-35°C. The measurements were done in the linear viscoelastic region (LVE) and a shear tension of 1 Pa was chosen from the rheological recordings.

Refractive index of PI solutions was measured on a Abbe refractometer at 25-35°C.

Interferometry experiments were performed on a Zeiss Interferometer to obtain the specific refractive index increments of the samples (dn/dc) in DMAc at 25°C.

CONCLUSIONS

Several solutions of some polyimides containing chalcogen atoms are analyzed in view of processing into reliable layers for solar cell shielding. It was made for the first time a correlation between shear oscillatory data and specific refractive index increment, showing that the polymer response to deformation and to light

interaction is dependent on the backbone flexibility in solvent environment. In addition, processing temperature is also reflected on the relaxation properties and it represents a factor of great interest during compounding of shielding layers for photovoltaic devices.

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