A very efficient and stable supramolecular organic blend having a very high value of the

optical gain for photorefractivity applications

A very efficient and stable supramolecular organic blend having a very high value of the optical gain for photorefractivity applications

R Angelone[1], F Ciardelli[1,2], A Colligiani[2,3,5], F Greco[1,2], P Masi[3], A Romano[3], G Ruggeri[1,2] and J L Stehlé[4]

1 Department of Chemistry and Industrial Chemistry, University of Pisa, 56126 Pisa, Italy
2 Istituto Nazionale per la Fisica della Materia, Polylab, 56100 Pisa, Italy
3 Department of Food Science, University of Napoli "Federico II", 80055 Portici (Napoli), Italy
4 SOPRA S A, 92270 Bois-Colombes, France

E-mail: colligia@dcci.unipi.it

Abstract. A derivative of 2-methylindole, 3-[2-(4-nitrophenyl)ethenyl]-1-allyl-2-methylindole, NPEMI-A, has been studied for its photoconductivity and photorefractivity behaviour. The neat material was studied together with its blends with the organic polymer poly-(2,3-dimethyl-N-vinylindole), PVDMI. It was possible to carry out measurements with the content of the chromophore NPEMI-A changing from zero to 100 wt. %. No opacity hint was observed. The photorefractive optical gain Γ_2 was obtained as a function of the chromophore content inside the different films. Differential Scanning Calorimetry measurements (DSC) were also carried out to obtain the whole change of the glass transition temperature T_g as a function of the amount of chromophore contained in the blends. From the experimental trend of T_g it was possible to gather a meaningful quantitative estimate of the value of the electrostatic interactions inside the blends. The importance of the value of T_g, and hence of the electrostatic interactions, in determining the extent of the photorefractivity has been clearly put in evidence. This was done by comparing the results obtained for NPEMI-A ($\Gamma_2 = 210.1$ cm^{-1}) with other ones previously discussed for a molecule similar to NPEMI-A but having a 2-ethylhexyl group, NPEMI-E ($\Gamma_2 = 2,027$ cm^{-1}), instead of an allyl group. Three different contributions to the photorefractivity of NPEMI-A, namely the Pockels, the Kerr and the Collaborative ones, could be distinguished from the peculiar trend of Γ_2 as a function of the composition of the blends.

1. Introduction

Electrooptical potentialities of photorefractive (PR) materials have been proved to be very promising tools in direct light amplification, reversible image and data recording and many other valuable and specialized applications [1]. In more recent years, the photorefractive effect has been particularly
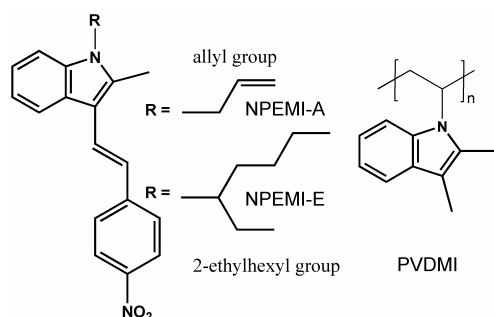
---

5 To whom any correspondence should be addressed.

studied in organic molecular substrates [2]. Organic PR materials offer the advantage that their components can be largely selected and modified to obtain specific electrooptical characteristics like the electric dipole moment (edm), the polarizabilities α and β, the first- and second-order susceptibilities [3]. Many organic molecules and blends have been synthesized and tested, but totally satisfactory results have been seldom recorded. A PR material, if it must be employed as a useful device (the PR cell), must possess at least two essential properties. The first one is the highest value of the photorefractive gain Γ_2. A high value of Γ_2 assures that the recorded data are represented by a high contrast hologram. The second property refers to the time durability of the cell (usually defined as shelf lifetime) that must maintain undefinitely its transparency without segregation of the chromophore. It begins to be clear that both properties can be rationalized also by thermodynamical considerations that take into account the so-called "free volume" of the polymer blend [4]. The chromophores are allowed to reorient under the effect of applied electric fields and their mutual electrostatic interactions. The possible reorientation gives origin to an important "birefringence contribution" (BR) to the photorefractivity[2]. The simultaneous presence of the electrostatic interactions can also further the sudden appearance of a "collaborative contribution" (COLL) that can strongly influence the PR behaviour. In this paper dealing with the NPEMI-A blends, we have quantitatively evaluated the different contributions to the photorefractivity. The results are compared with those previously obtained for NPEMI-E [5], ($\Gamma_2 = 2,027$ cm^{-1}), by rationalizing the different values of T_g of the two series of blends. The value of T_g, strictly connected to the value of the electrostatic interactions, has been found to be perhaps the most important factor conditioning both the value of Γ_2 and the shelf lifetime of the studied blend. We conclude by confirming that the aim of our research in this field is chiefly sustained by the effort to rationalize the ultimate factors that can optimize the technological applications of the photorefractive materials in more and more efficient devices.

2. Chemicals

Figure 1 reports the molecular structures of the two chromophores that we have taken into consideration. NPEMI-A is the already cited 3-[2-(4-nitrophenyl)ethenyl]-1-allyl-2-methylindole while NPEMI-E is 3-[2-(4-nitrophenyl)ethenyl]-1-(2-ethylhexyl)-2-methylindole. The repetitive unit of PVDMI, the second component of the blend, is also shown. The syntheses of both NPEMI-E and PVDMI have already been reported [5,6]. The synthesis of NPEMI-A follows a very similar route and will be published elsewhere.

Table 1. The experimental values of the glass transition temperature T_g, of the photocurrent i_{ph} and of the photorefractive gain Γ_2 for a part of the studied NPEMI-A blends.

Blend	T_g (°C)	i_{ph} (A) [a]	Γ_2 (cm^{-1}) [a]
NPA50 [b]	49.9	2.92 x 10^{-8}	3.4
NPA70	33.1	6.50 x 10^{-8}	23.5
NPA75	29.3	8.27 x 10^{-8}	40.2
NPA80	26.7	1.06 x 10^{-7}	59.8
NPA85	23.9	1.15 x 10^{-7}	85.5
NPA90	22.0	1.06 x 10^{-7}	115.4
NPA95	19.8	1.45 x 10^{-7}	120.9
NPA99	18.4	2.40 x 10^{-7}	210.1

[a] At E = 75 V/μm
[b] NPA ≡ NPEMI-A

Figure 1. The molecular structures of NPEMI-A, NPEMI-E and of the repetitive unit of poly-(2,3-dimethyl-N-vinylindole), PVDMI.

A third component, 2,4,7-trinitrofluorenylidenemalononitrile (TNFM) is always present in each blend at a fixed wt. % = 1 amount. It plays the role of the "sensitizer"[2].

3. Methodologies

3.1. Electrooptic and Calorimetric (DSC) measurements
Photorefractivity was measured by the "asymmetric two-beam coupling" (2BC) method [1,2]. The two laser beams at λ = 685 nm were obtained from a solid state laser. The photorefractive optical gain Γ_2 is referred to the "signal" beam named 2. The photocurrent i_{ph} was measured by using a single laser beam.
A Perkin Elmer DSC7 Calorimeter was used. Neat NPEMI-A had a melting point T_m = 122.0°C and a glass transition temperature T_g = 18.4°C. These values have to be compared with the corresponding values found for NPEMI-E that amounted to T_m = 68.0°C and T_g = -2.5°C [5].

4. Results

4.1. Differential Scanning Calorimetry
Table 1 reports the measured values of T_g, i_{ph} and Γ_2. For NPEMI-A blends a value of the mixing enthalpy ΔH_m = -3.3 kJ mol^{-1} is obtained that is more negative than ΔH_m = -2.5 kJ mol^{-1} obtained for NPEMI-E blends [5,7]. Therefore, intermolecular electrostatic interactions are larger for NPEMI-A blends. The values of T_g allow to classify NPEMI-E as a "soft" material while NPEMI-A is at the border between the "soft" and the "hard" materials [4].

4.2. Photoconductivity and photorefractivity
Table 1 reports the values of the measured i_{ph} at E = 75 V/μm. The existence of the "Collaborative effect" [8], for the first time detected with NPEMI-E [5], is confirmed also in NPEMI-A blends by a clear minimum[9] at about wt.% = 90. Table 1 and Figure 2 report the values of the photorefractive optical gain Γ_2. The very peculiar trend of Γ_2 obtained at E = 75 V/μm (full dots) allows to distinguish for the first time, at our knowledge, the three main contributions that establish the value of the modulation Δn of the local refractive index n to which Γ_2 is proportional. The three main contributions that determine the value of Δn are [2] the electrooptical, the reorientational and the collaborative one as the hump in the experimental trend seems to suggest. To separate these contributions we have tried a semiempirical deconvolution of the experimental trend. The deconvolution was succesfully possible as shown in figure 2. It is important to stress that, when we compare the photorefractive performances at the same value of $T_r = T_g - T_{rt}$ (i.e. the distance of T_g from rt) at which T_g of the respective blend has the same value , NPEMI-A results to be more efficient than NPEMI-E.
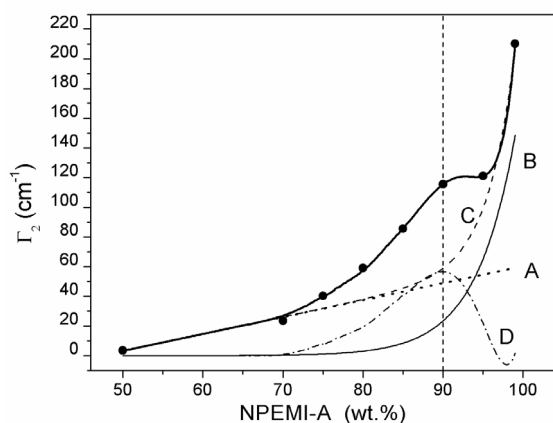
Figure 2. The trend of the measured values of Γ_2 at E = 75 V/μm and at rt as a function of the NPEMI-A content (full dots); the broad line is a polynomial function that must be considered only an aid for the eye. All other lines are semiempirical deconvolution functions of the experimental trend. They represent: A, the Pockels contribution; B, the Kerr contribution; C, the sum of the two contributions; D, the Collaborative contribution.

The rapid increase of Γ_2 for NPEMI-A contents higher than 90, contrary to what happened with NPEMI-E, can be rationalized starting from the concept of "traps" [2,10]. A trap can be defined as a site where a migrating charge can be captured contributing to form the charge lattice from which the space-carge field E_{SC} generates. Γ_2 is proportional to E_{SC} that in turn increases its value when the density of traps N_T increases [11]. The traps can be classified as "soft" and "deep" species depending on T_g and their electrostatic depth. When the value of T_g decreases, the traps become more and more of the soft type, i.e. easily thermally excitable and short-living. For this reason Γ_2 of NPEMI-E decreased while that of NPEMI-A continues to increase due to its higher T_g value.

As a last but not least remark, we can assert perhaps in a more safe way than in the case of NPEMI-E, that neat NPEMI-A has no tendency to couple in front-to-back dimers with edm = 0, that cannot be active species for the photorefractive effect [3]. This is clearly demonstrated by the increasing trend of the optical gain up to $\Gamma_2 = 210.0$ cm^{-1}, figure 4.

5. Conclusions

The study of photoconductivity and photorefractivity of NPEMI-A and of its blends allowed to confirm the existence of the "Collaborative effect". We have shown that this effect conditions, together with the usually observed electrooptical and reorientational effects, the photoconductive behaviour. From the measurements here reported it was possible to quantitatively evaluate the respective contribution of each effect. This possibility can furnish important suggestions on how to obtain blends or neat materials having very high photorefractive optical gains Γ_2. NPEMI-A, that we have studied here, might have, in similar conditions of T_r, a value of Γ_2 even higher than that of NPEMI-E. We remember that in a previous study [5] concerning a similar molecule, NPEMI-E, we already measured a $\Gamma_2 = 2{,}027$ cm^{-1}. The DSC study that was possible on a complete series of blends containing the chromophore in wt.% content changing from 0 to 100, allowed to confirm the importance of $T_r = T_g - T_{rt}$ for each material taken into consideration. The information obtained on the value of electrostatic intermolecular interactions justifies the complete stability of the obtained photorefractive cells that maintain undefinitely their transparency even for the neat material.

References

[1]   Solymar L, Webb D J and Grunnet-Jepsen A 1996 *The Physics and Applications of Photorefractive Materials* (Oxford: Clarendon Press–Oxford University Press)

[2]   Ostroverkhova O and Moerner W E 2004 *Chem. Rev.* **104** 3267

[3]   Kippelen B, Meyers F, Peyghambarian N and Marder S R 1997 *J. Am. Chem. Soc.* **119**, 4559
       Würthner F, Wortmann R and Meerholz K 2002 *CHEMPHYSCHEM* **3** 17

[4]   Van Krevelen D W 1997 *Properties of Polymers* (North Holland: Elsevier)

[5]   Angelone R, Angiuli M, Ciardelli F, Colligiani A, Greco F, Romano A, Ruggeri G and Tombari E 2006 *Organic Optoelectronics and Photonics II (Proc. SPIE* vol 6192) ed Heremans P L, Muccini M and Meulenkamp E A (Bellingham: SPIE) pp 61922M1-12
       Angelone R, Ciardelli F, Colligiani A, Greco F, Masi P, Romano A, Ruggeri G and Stehlé J L 2008 *Appl. Opt.* **47** 6680

[6]   Brustolin F, Castelvetro V, Ciardelli F, Ruggeri G and Colligiani A 2001 *J. Polym. Sci. A Polym. Chem.* **39** 253

[7]   Lu X and Weiss R A 1991 *Macromolecules* **24** 4381
       Flory P J 1953 *Principles of Polymer Chemistry* (Ithaca: Cornell University Press)

[8]   Terenziani F and Painelli A 2003 *Phys. Rev. B* **68** 165405

[9]   Pai D M, Yanus J F and Stolka M 1984 *J. Phys. Chem.* **88** 4714

[10]   Young R H, Sinicropi J A and Fitzgerald J J 1995 *J. Phys. Chem.* **99** 9497

[11]   Ostroverkhova O, He M, Twieg R J and Moerner W E 2003 *CHEMPHYSCHEM* **4** 732