Effect of electrical poling on conductivity in guest-host polymers

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A comparative study on 4-N,N'-dimethylamino-3- acetamidonitrobenzene (DAN) doped polycarbonate (PC) and DAN doped poly-methyl-methacrylate (PMMA) shows that electrical poling enhances electrical conductivity. This enhancement is mainly due to the interaction between the guest molecules and the host polymers. In this work it has been found that the increase in conductivity is higher in DAN/PC than in DAN/PMMA. This is due to the hydrogen bonding which occurs between the carbonyl group of PC and the nitro group of DAN. Hydrogen bonding enhances also the poling efficiency of DAN molecules in PC. Besides the increase of the magnitude of the electrical conductivity, a hysteresis loop is obtained.

1. Introduction

Electrical, optical, mechanical and thermal properties of polymers have been investigated by many researchers for decades in order to explore better materials for technological use. Polymeric materials are used for photonics and for integrated optical applications. It is now a well-established technology since polymeric materials are used in modulators, switchers, amplifiers and detectors. Polymeric materials find application also in optical communication systems as an active layer of waveguides [1-2].

The poled electro-optic (EO) polymers have applications in the generation and the detection of terahertz (THz) radiation [3-4]. Since the THz signals have energies of about 1 meV, and since unlike x-rays these signals are not ionic, they can be used in medical imaging without harming biological tissues. The THz spectroscopy can also be used in the study of carrier dynamics…

A lot of interest has been shown in the recent years to electrical conductivity in polymers. As a result of the intensive research in this field, great developments have been made in many areas such as information technology, where devices of great speed, reduced sizes and weights have been designed.

Experimentally, it has been proven that doping guest molecules into amorphous polymers hosts increases electrical conductivity. For example, it has been reported in some of the early works on this topic [5] that the selective chemical oxidation of a fraction of the transport molecules increases the dc electrical conductivity of several orders of magnitude. Danz et al. have reported that the incorporation of plasticizers increases both the mobility, and dipolar orientation and polarization in the polymer structure [6].

It has been reported that the doping of molecules into crystal solutions during crystal growth improves optical properties of crystal materials. For instance, the doping of L-proline into KDP solutions improves optical transmittance and enhances NLO properties [7].

In addition, it is realized that the poling of β-poly(vinylidene fluoride) causes an enormous increase in conductivity, especially at high temperatures [8]. This increase in conductivity is ascribed mainly to the hopping process which is due to the free charges induced during the poling [8]. Induced alignment in one direction of molecules that have a conjugated long π chain sandwiched between electron donating and accepting end groups (D-π-A), in guest-host (G-H) systems, increases also the conductivity [7, 8]. When G-H systems are first prepared, guest molecules are randomly orientated. By the poling process these molecules get aligned in the field direction, in a road-like fashion. This explains how the alignment of these D-π-A guest molecules in the charge transfer direction contributes to the increase of the conductivity.

In this work DAN guest molecules are incorporated into PMMA and PC amorphous polymers and the conductivity of poled samples are compared to that of the unpoled ones. It is noticed that the conductivity is greatly enhanced by the poling process. Thin films of G-H polymers are poled by a thermal poling process, and the conductivity of poled and unpoled samples are measured with Keithley 617 electrometer.

2. Sample preparation

The preparation of the samples used in this work is as follows: DAN molecules and polymers are dissolved in dichloromethane. 20% w/w DAN/polymer solutions are prepared. The solutions are filtered to remove undissolved contaminants. Thin films of each polymer systems are prepared by the dip coating technique. In order to prepare 2-4 μm thick films, ITO glass slides are withdrawn from

the solution with a certain speed. Films are dried in an oven under vacuum at 100 °C for an hour. The chemical structures of 4-N, N'-dimethylamino-3-acetamidonitrobenzene (DAN), poly(methyl)methacrylate (PMMA) and polycarbonate (PC) are shown in Fig. 1.
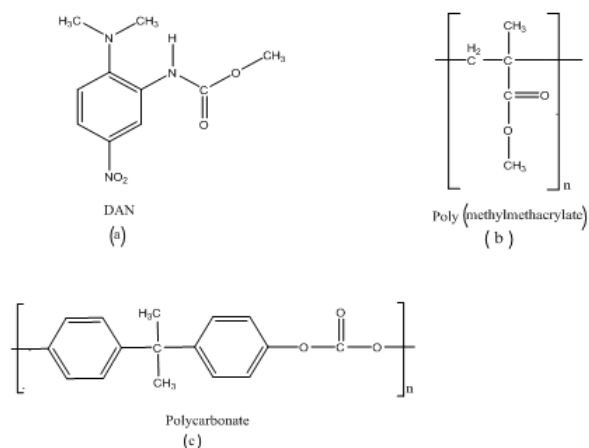

Fig. 1. Chemical structures of materials used.(a) 4-N, N'-dimethylamino - 3 - acetamidonitrobenzene (DAN) guest molecules, (b) PMMA and (c) PC host polymers.

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3. Electrical poling

Thin films are poled through corona discharge poling. A needle is kept 1.5 cm above the sample, and 5 - 8 kV fields are applied to the needle. The samples are heated gradually to the poling temperature for 15 minutes. Then the samples are kept at this temperature for 5 minutes. While the field is on, the temperature is reduced to room temperature in 45 minutes. The poling temperature is 70 °C for DAN/PMMA and 90 °C for DAN/PC samples. These temperatures are chosen because they are close to the Tg of the samples. In our previous work we observed a reduction in Tg of the polycarbonate host from 150 °C in the undoped form, to around 90 °C when loaded to 20% w/w with DAN [9]. Long cooling time permitted the reduction of the free volume in the samples which contributes to the enhancement of the stability of polar induced alignment [10].

Space charges can affect the temporal stability of poled polymers and also may cause a reduction of the absolute value of the field applied to the polymer sample. In order to improve the poling efficiency, a TiO_2 barrier layer was spin coated on the ITO substrate. Since TiO_2 has a high electrical conductivity and a large dielectric constant, it reduces the space charge injection into the polymer, which allows the absolute poling voltage to be applied effectively across the active polymer layer [11-12]. A 40 % enhancement in the poling efficiency was obtained with the TiO_2 coated sample, when compared to the poled samples without the barrier layer. Thus ultra large E-O

coefficients, up to 160-350 pm/V at 1310 nm, have been obtained [11, 12].

4. Results and discussion

As it is seen in Fig. 2, compared to the undoped PC, a hysteresis-like variation of the current is obtained when DAN guest molecules are doped into the PC host polymer. The conductivity in this sort of materials is usually explained by the hopping process. Therefore, as the concentration of dopant gets higher, charges can easily jump from one site to another, which leads to an increase in conductivity.
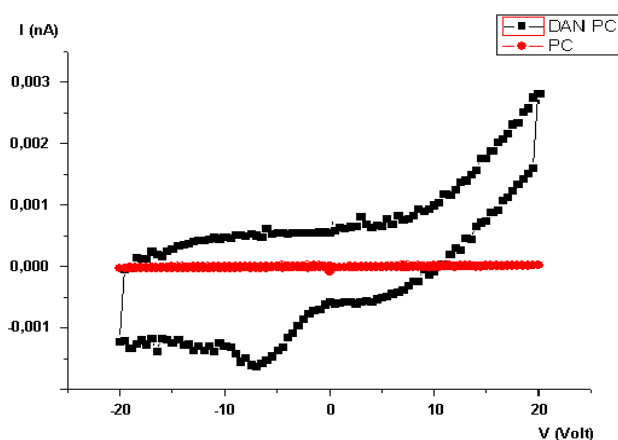

Fig. 2. I-V characteristics of undoped and doped PC.

The thermal poling aligns the molecules of dopants in the field direction, which are previously randomly oriented, in the polymer matrix. This indicates that the poling can also increase the conductivity. In order to prove this, DAN doped PC and PMMA samples were poled, and their I-V characteristics were compared to those of unpoled samples. The results of this comparison are shown in Fig. 3 and Fig. 4.
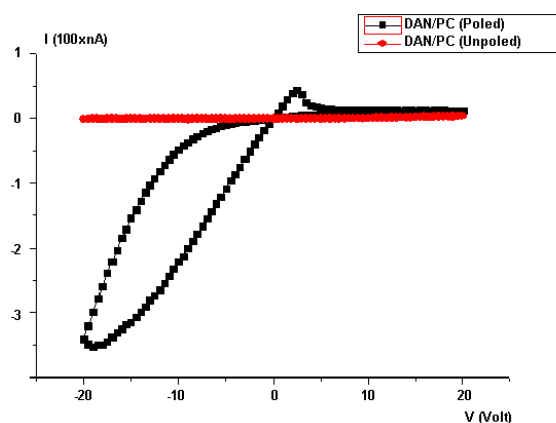

Fig. 3. I-V characteristics of unpoled and poled DAN/PC samples.

As one can see from this figure, the current response of the poled sample is different to that of the unpoled one; both in value and in character. When a dc field in the range of - 20 to +20 V is applied to the unpoled sample, almost no current crosses it. But when the same field is applied to the poled sample, a higher current response is obtained. For a 20 V applied field, a current of the level of 10^{-12} A is obtained for the unpoled DAN/PC sample, as shown in Fig. 2, whereas a current of the level of 10^{-7} A is obtained for the poled sample, for the same voltage, as shown in Fig. 3. Thus an increase of five orders of magnitude in the current is obtained for the poled sample. This increase of the current implies that the conductivity is greatly improved by poling.

During poling, space charges are generated and this reduces the effectiveness of the poling field. In order to eliminate the effect of the space charges which occurs during corona discharge, the conductivity measurements are carried out a few days after poling. Since a complete relaxation occurs in DAN/PMMA sample in 24 hours [13], no current is observed for a 20 V applied field. This shows that space charges are eliminated.

Although there is almost no response for the applied positive field, a noteworthy current response in the form of a hysteresis loop is obtained for the negative field, which implies that the current response is polarity dependent. It also shows that DAN molecules have permanent poling induced alignment in the PC host.

As it is mentioned above, delocalized π conjugated dipolar structure of the molecules in this G-H system, and the alignment of these molecules in the charge transfer direction explain both the increase in conductivity and its polarity dependent behavior.

Also the I-V characteristics of the same guest molecules doped into a different polymer (PMMA) sample were considered and compared with those of the previous sample. Both samples were poled under the same poling conditions. The I-V characteristics of these two poled samples are depicted in Fig. 4.
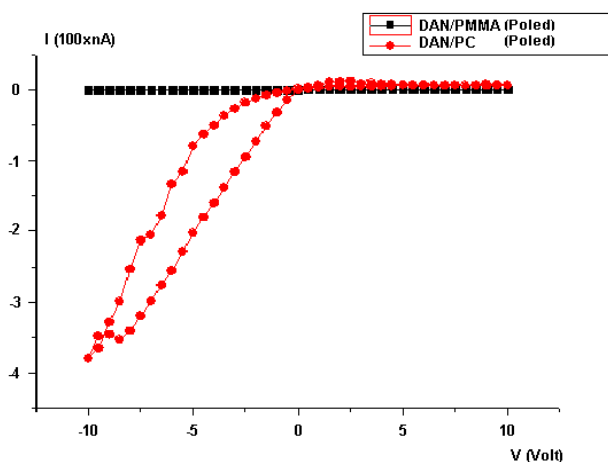
As it is seen in Fig. 4, there is almost no current response in the case of poled DAN/PMMA sample in the range of - 10 to +10 V applied field. This result is expected since the I- V measurements have been carried out a few days after poling. As for the DAN/PC sample, a similar current response to the one in Fig. 3 is obtained, which confirms these results. Again in the negative voltage range, a current response in the form of a hysteresis is seen, and there is almost no current response for the positive voltages. This is actually another evidence of permanent polar alignment of DAN guest molecules in PC host polymer matrix.

A further confirmation of these characteristics is the results obtained in our previous work [13]. The measured r_{33} coefficient of poled DAN/PC was 10 times greater than that of the poled DAN/PMMA, and the polar induced alignment in the first sample was much more stable than in the second one. Although a complete relaxation occurred just in 24 hours for the DAN/PMMA sample, only 30 % relaxation occurred for DAN/PC in three months [13]. All these results show that the poling efficiency of the DAN/PC sample is much higher than that of the DAN/PMMA, and the first sample is a stable material. This stability shows that the enhancement in the conductivity becomes a permanent property of DAN/PC.

In reference [14], IR spectrum of these two samples shows that a stronger hydrogen bonding occurs between DAN molecules and PC host. This is one of the factors that explain the better stability obtained in DAN/PC. Here the hydrogen bonding which occurs between the nitro group of DAN and the carbonyl group of PC causes π-π stacking between guest molecules and the host polymer. This interaction is presumably the main factor responsible for the increase in the conductivity, because when a guest molecule is bound to a host polymer chain, it can be said that charge transition becomes easier. But we should bear in mind that this cannot be the only factor that improves the conductivity this much. It has been shown that PC is itself a polar electret [15] that contributes also to the increase of the current. However, the same thing cannot be said for PMMA [13]. Since PMMA does not contain aromatic groups, π-π stacking is lacking in DAN/PMMA.

The following plot shows the effect of the temperature on the conductivity for both poled and unpoled DAN/PC. In this figure, the current increase in the unpoled sample starts around 70 °C, and increases sharply close to Tg. As for the poled sample, up to the temperature of 100 °C no current increase is observed. Over this temperature, the increase in the current of the poled sample is comparatively very small. This result confirms further that the poled DAN/PC sample is stable even at high temperatures.
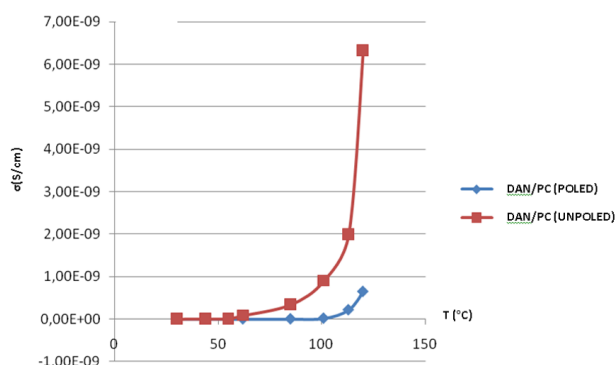

Fig. 4. I-V characteristics of poled DAN/PMMA and
DAN/PC samples.

Fig. 5. Temperature-conductivity relationship of poled and unpoled DAN/PC samples.

5. Conclusion

In this work, the effect of thermal poling on the dc conductivity of guest-host systems is investigated. According to the results obtained from two different G-H systems, the poling increases the conductivity in both cases. However, this increase in the conductivity depends on the interaction between guest molecules and host polymers. In the samples where the hydrogen bonding occurs between the guest molecules and the polymer host such as DAN/PC, a considerable increase in conductivity is obtained. Poled DAN/PC thin films shows a diode characteristics.

Poled EO polymers which have low optical loss and relatively high electrical conductivity may increase the effectiveness of THz signal generation. If poled EO polymers are in the waveguide form, the nonlinear frequency conversion efficiency enhances greatly.

References

[1] Y. Enami, C. T. Derose, D. Mathine, C. Loychik, C. Greenlee, R. A. Norwood, T. D. Kim, J. Luo, Y. Tian, A. K.-Y. Je, N. Peyghambarian, Nat. Photonics **1**, 180 (2007).
[2] C. Y. Lin, X. Wang, S. Chakravarty, B. S. Lee, W. Lai, Appl. Phys. Lett. **97**, 093304 (2010).
[3] H. Cao, T. F. Heinz, A. Nahata, opt. Lett., **27**(9) 775 (2002).
[4] A. M. Sinyukov, M. R. Leah, L. M. Hayden, M. H. J. Luo, A. K.-Y. Jen, L. R. Dalton, Appl. Phys. Lett. **85**(24) 5827 (2004).
[5] J. Mort, S. Grammatica, D. J. Sandman, A. Troup, J. of Electronical Materials. **9(2)**, 411 (1980).
[6] R. Danz, B Elling, W. KünstIer, M. Pinnow, R. Schmolke, A. Wedel, D. Geib, IEEE T Dielect El In, **25**(2), 325 (1992).
[7] P. Jagdish, N. P. Rajesh, J. Optoelectron Adv. Mater. 13966 (2011).
[8] V. Sencadas, C. M. Costa, V. Moreira, J. Monteiro, S. K. Mendiratta, J. F. Mano, S. Lanceros-Méndez, E-Polymers, **002**, 1 (2005).
[9] D. Bloor G. H. Cross, Y. Karakus, D. Gray, OMNO, Oxford, UK, 1993, p. 182.
[10] H. L. Hampsch, J. Yang, G. K. Wong, J. M. Torkelson, Macromolecules **23**, 3648 (1990).
[11] S. Huang, T. D. Kim, J. Luo, S. K. Hau, Z. Shi, X. H. Zhou, H. L. Yip, A. K. Y. Jen, Appl. Phys. Lett. **96**, 243311 (2010).
[12] S. Huang, J. Luo, Z. Jin, X. H. Zhou, Z. Shi, A. K. Y. Jen, J. Mater. Chem., **22**, 20353 (2012).
[13] Y. Karakus, D. Bloor, G. H. Cross, J. Phys. D: Appl. Phys. **25**, 1014 (1992).
[14] D. Healy, D. Bloor, D. Gray, G. H. Cross, J. Phys. D: Appl. Phys. **30**, 3079 (1997).
[15] R. J. Gulloty, C. A. Langhoff, S. E. Bales, Proc. SPIE, **1337**, 258 (1990).

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