ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2016, **26**, 518–520

Mendeleev Communications

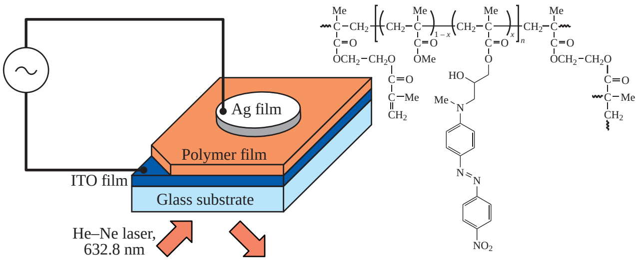
Measurements of the electro-optic coefficients of polymer films based on branched methacrylic copolymers containing azo chromophores

Maksim A. Smirnov,*[a] Anvar S. Mukhtarov,[a] Natalia V. Ivanova,[a] Tatyana A. Vakhonina,[a,b] Gul'shat N. Nazmieva,*[a] Irek R. Nizameev,[a,b] Valery V. Bazarov,[c] Marina Yu. Balakina[a] and Oleg G. Sinyashin[a]

[a] *A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences, 420088 Kazan, Russian Federation. E-mail: macs-ne@mail.ru, gulshat.nazmieva@yandex.ru*
[b] *Kazan National Research Technological University, 420015 Kazan, Russian Federation*
[c] *E. K. Zavoisky Physical-Technical Institute, Kazan Scientific Center of the Russian Academy of Sciences, 420029 Kazan, Russian Federation*

DOI: 10.1016/j.mencom.2016.11.020

The electro-optic coefficients of 20, 33 and 21 pm V^{-1} for branched methacrylic copolymers FI, FII and FIII, respectively, with different chromophore contents were determined by a Teng–Man ellipsometric technique.



Organic polymeric materials exhibiting a nonlinear optical (NLO) response to an applied high-intensity electrical field have been extensively studied. In particular, materials with a linear electro-optic (EO) response (Pockels effect) were obtained to be applied in photonic and optoelectronic devices, optical modulators and THz switches to increase data processing speeds by several orders of magnitude, as compared to that of electronic processes.[1,2] Due to the high values of EO coefficients, r_{33}, low values of dielectric constant and its small dispersion, good processability and compatibility with diverse materials (metals, silicon, silica, *etc.*) organic NLO polymers can be considered more preferable than traditional inorganic materials such as $LiNbO_3$. The key requirement in the development of such materials is the temporal and thermal stability of EO responses.

The molecular sources of polymer NLO properties are organic chromophores, in particular, dipolar molecules end capped with electron donor and electron acceptor groups connected by a conjugated π-electron bridge. Chromophores are characterized by high dipole moment and first hyperpolarizability; they are either introduced into a polymer matrix as guest molecules or covalently attached to the side/main chain of the polymer.

The NLO polymer EO coefficient depends on the concentration of chromophore groups (N), first hyperpolarizability (β_{zzz}), defining the effect at the molecular level, the orientation of the chromophores that determines noncentrosymmetric organization in the polymeric matrix $\langle\cos^3\theta\rangle$:[3]

$$r_{33} = N\langle\cos^3\theta\rangle\frac{2\beta_{zzz}(\omega)F(\omega)}{n^4}, \qquad (1)$$

where n is the material refraction index, and F is a coefficient that depends on local field factors. However, this simple linear dependence of r_{33} on N holds only at low chromophore concentrations in a matrix; when N exceeds some threshold value, this dependence becomes nonlinear because of the aggregation of chromophores.[4]

One of the ways to introduce chromophores into a material for the better relaxation stability of an EO response in comparison with composite materials is their covalent attachment to the polymer backbone. To increase the chromophore concentration and avoid undesirable dipole–dipole interaction between them leading to aggregation and a decrease of EO characteristics, it was proposed to use dendritic chromophore-containing polymers[5,6] and branched polymer structures, which provide the spatial separation of chromophores.[7–9]

Earlier, we studied the NLO characteristics of linear methacrylic copolymers with azo chromophores in the side chain.[10] Here, we present the results of the measurements of the EO coefficients of polymer films based on branched methacrylic copolymers with different chromophore contents: 14 mol% (**FI**), 21 mol% (**FII**) and 29 mol% (**FIII**) (Figure 1). The test polymers were synthesized using a procedure described elsewhere.[9] The chromo-

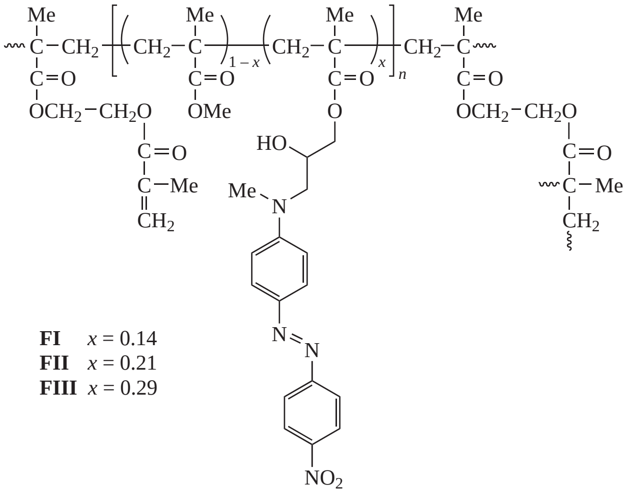


Figure 1 Structural formula of the branched methacrylic copolymers.

Table 1 Characteristics of the polymer films.

Film	Chromophore concentration (mol%)	$N/10^{20}$ cm^{-3}	T_g/°C	T_p/°C	d/nm	σ/nm (before/after poling)	η	$r_{33}{}^a$/pm V^{-1}
FI	14	5.42	94	106	900	17/33	0.07	20(2)
FII	21	7.88	105	115	800		0.19	33(3)
FIII	29	10.12	113	127	815	4/12	0.17	21(2)

[a] The measurement uncertainty is given in parentheses.

phore content was estimated by NMR and elemental analysis.[9] The glass transition temperatures T_g of polymers **FI**, **FII** and **FIII** were determined by DSC (94, 105 and 113 °C, respectively).

The development of an EO cell for the measurement of the EO coefficients of the test films consists of three stages. First, thin polymer films were prepared on glass plates 1 mm thick coated with a transparent conducting indium tin oxide (ITO) film using a 15% polymer solution in cyclohexanone by a spin-coating procedure (~5000 rpm for 45 s).[9] Then, the samples were cured in a vacuum oven at room temperature for 10 to 16 h followed by heating to 50 °C for 2 h to remove a residual solvent. The thickness (d) and roughness (σ) of the obtained films were controlled by an AFM technique; the values of d and σ are presented in Table 1.

The second stage consisted in the orientation of the chromophores along the applied electric field direction to achieve a noncentrosymmetric structure of the material, which is necessary for detecting a linear EO response (a chromophore poling procedure). In the case of the test polymer films, the poling was carried out using a home-made corona triode setup and a so-called positive corona.[11] The voltage on the needle tungsten electrode was 8 kV; the distance from the grid to the cathode was 10 mm, and the grid voltage was 1.2 kV. Corona field was applied to the samples heated to the poling temperature T_p, which is higher than the T_g of the polymer. After 20 min, the sample was cooled to room temperature; then, the field was switched off. The optical absorption of the films was detected using a Perkin–Elmer Lambda 35 UV/Vis spectrometer before (see Figure 2) and after poling. The degree of orientation is controlled by the order parameter η:

$$\eta = 1 - A/A_0, \qquad (2)$$

where A_0 and A are the optical absorptions of a film before and after poling, respectively. According to the AFM data, the poling process results in the modification of the film surface and an essential increase in the film roughness (Figure 3, Table 1).

The third stage of EO cell fabrication is the deposition of a thin silver film (the second electrode) with a diameter (D) of 6 mm and a thickness of ~30 nm on the surface of the polymer film by thermal evaporation. The ITO film served as the first electrode.

The EO coefficients r_{33} were measured by a Teng–Man technique[12] on a home-made setup (He–Ne laser; λ = 632.8 nm).[13] The refractive index n for the polymer films was taken equal to 1.6.[14] Table 1 summarizes the results of the measurements and some characteristics of the films and parameters of the poling process.

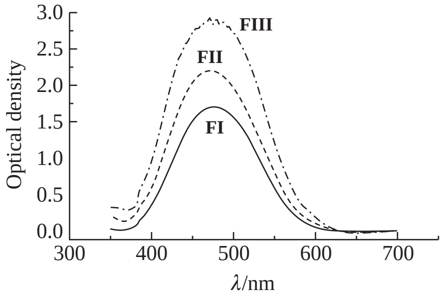


Figure 2 The UV-VIS spectrum of **FI**, **FII** and **FIII** before poling.

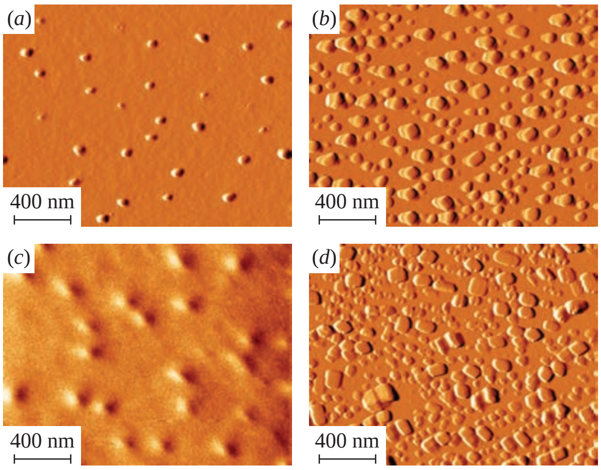


Figure 3 Film surfaces of (*a*, *c*) **FI** and (*b*, *d*) **FIII** (*a*, *b*) before and (*c*, *d*) after poling.

Earlier, we found that r_{33} of linear methacrylic copolymers with chromophores in the side chain, MMA-MAZ, is 27 pm V^{-1} (λ = 632.8 nm) at a chromophore content of 26 mol%,[13] and d_{33} for the polymer with a chromophore content of 17 mol% is 60 pm V^{-1} (λ = 1064 nm).[15] For methacrylic polymers PMMA-DR1 having a similar structure and containing azo chromophores in the side chain, the values of r_{33} = 18 pm V^{-1} (λ = 632.8 nm)[16] and 20.9 pm V^{-1} (λ = 670 nm)[17] and d_{33} = 43 pm V^{-1} (λ = 1064 nm)[16] were reported. Thus, the values of EO and NLO coefficients obtained for MMA-MAZ, are about 1.5 times higher than the published values. This discrepancy may be due to both a difference in the structures of the polymer matrices and the way of polymer film poling: a contact method (parallel electrodes) was used[16] for the orientation of chromophore groups, which is known to result in less effective poling than that with a corona discharge.[3] The data of Table 1 show that the branched polymers exhibit the values of r_{33} comparable with those for MMA-MAZ;[13] for **FI** and **FIII**, the values of EO coefficients are almost the same in spite of different chromophore contents. As for **FII**, the obtained value of r_{33} is essentially higher (by approximately 65%); thus, the chromophore content is close to an optimal one in this case. In **FI**, the concentration of chromophores is low, while the aggregation of chromophores in **FIII** seems to occur as chromophore concentration in the polymer is rather high in this case.

Therefore, the data obtained give evidence that branched methacrylic copolymers are promising for the development of EO materials; further research will be directed to study the temporal and thermal stability of material EO responses.

This work was supported by the Russian Science Foundation (grant no. 16-13-10215) .

Microscopic investigations were carried out in the Spectroscopy, Microscopy and Thermal Analysis laboratory of Kazan National Research Technological University; we are grateful to Professor E. S. Nefed’ev.

References

1 L. R. Dalton, *J. Phys.: Condens. Matter*, 2003, **15**, 897.
2 L. R. Dalton, P. A. Sullivan and D. H. Bale, *Chem. Rev.*, 2010, **110**, 25.
3 D. M. Burland, R. D. Miller and C. A. Walsh, *Chem. Rev*., 1994, **94**, 31.
4 M. Yu. Balakina, *ChemPhysChem*, 2012, **13**, 4186.
5 H. Ma and A. K.-Y. Jen, *Adv. Mater*., 2001, **13**, 1201.
6 G. N. Nazmieva, T. A. Vakhonina, S. M. Sharipova, N. V. Ivanova, A. Sh. Mukhtarov, M. A. Smirnov, M. Yu. Balakina and O. G. Sinyashin, *Mendeleev Commun.*, 2015, **25**, 101.
7 Z. Zhu, Z. Li, Y. Tan, Z. Li, Q. Li and Q. Zeng, *Polymer*, 2006, **47**, 7881.
8 Z. Li, Q. Li and J. Qin, *Polym. Chem.*, 2011, **2**, 2723.
9 T. A. Vakhonina, M. Yu. Balakina, G. N. Nazmieva, N. V. Ivanova, S. V. Kurmaz, I. S. Kochneva, M. L. Bubnova, E. O. Perepelitsina, N. N. Smirnov, A. V. Yakimansky and O. G. Sinyashin, *Eur. Polym. J*., 2014, **50**, 158.
10 T. A. Vakhonina, N. V. Ivanova, N. N. Smirnov, A. V. Yakimansky, M. Yu. Balakina and O. G. Sinyashin, *Mendeleev Commun*., 2014, **24**, 138.
11 J. A. Giacometti and O. N. Oliveira, *IEEE Trans. Electr. Insul*., 1992, **27**, 924.
12 C. C. Teng and H. T. Man, *Appl. Phys. Lett*., 1990, **56**, 1734.
13 M. A. Smirnov, A. S. Mukhtarov, N. V. Ivanova, T. A. Vakhonina, V. V. Bazarov and M. Yu. Balakina, *XIX International Youth Scientific School ‘Coherent Optics and Optical Spectroscopy’*, 2015, Kazan, p. 182.
14 *Characterization Techniques and Tabulations for Organic Nonlinear Optical Materials*, eds. M. G. Kuzyk and K. W. Dirk, Marcel Dekker, New York, 1998.
15 M. A. Smirnov, A. S. Mukhtarov, N. V. Ivanova, T. A. Vakhonina, V. V. Semashko and M. Yu. Balakina, *J. Phys. Conf. Ser*., 2014, **560**, 012015.
16 Y. Shuto, M. Amano and T. Kaino, *Jpn. J. Appl. Phys.*, 1991, **30**, 320.
17 P. Nagtegaele, E. Brasselet and J. Zyss, *J. Opt. Soc. Am. B: Opt. Phys.*, 2003, **20**, 1922.

Received: 5th April 2016; Com. 16/4900