

## Synthesis and characterization of polyacrylates containing charge transfer groups

Min Li<sup>1,\*</sup>, Enle Zhou<sup>1</sup>, Jiping Xu<sup>1</sup>, Chuncal Yang<sup>2</sup>, Xinying Tang<sup>2</sup>

<sup>1</sup> Polymer Physics Laboratory of Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

<sup>2</sup> Department of Chemistry, Jilin University, Changchun 130023, People's Republic of China

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### Summary

Polyacrylates containing para-nitro azobenzene have been synthesized by free radical polymerization. The influence of the length of the spacer of the homopolyacrylates (HP<sub>n</sub>, n=3,4,6), content of methyl acrylate in the copolyacrylates (CP6) with para-nitro azobenzene groups on the thermal properties, such as liquid crystallinity, T<sub>g</sub> and T<sub>m</sub>, was studied by DSC, WAXD and polarized optical microscopy. Among the polymers studied, only the homopolyacrylate (HP6) with six carbon atoms in the spacer exhibited a nematic phase. The second-harmonic generation (SHG) signal of the poled HP6 film was detected qualitatively by Maker-fringer method.

### Introduction

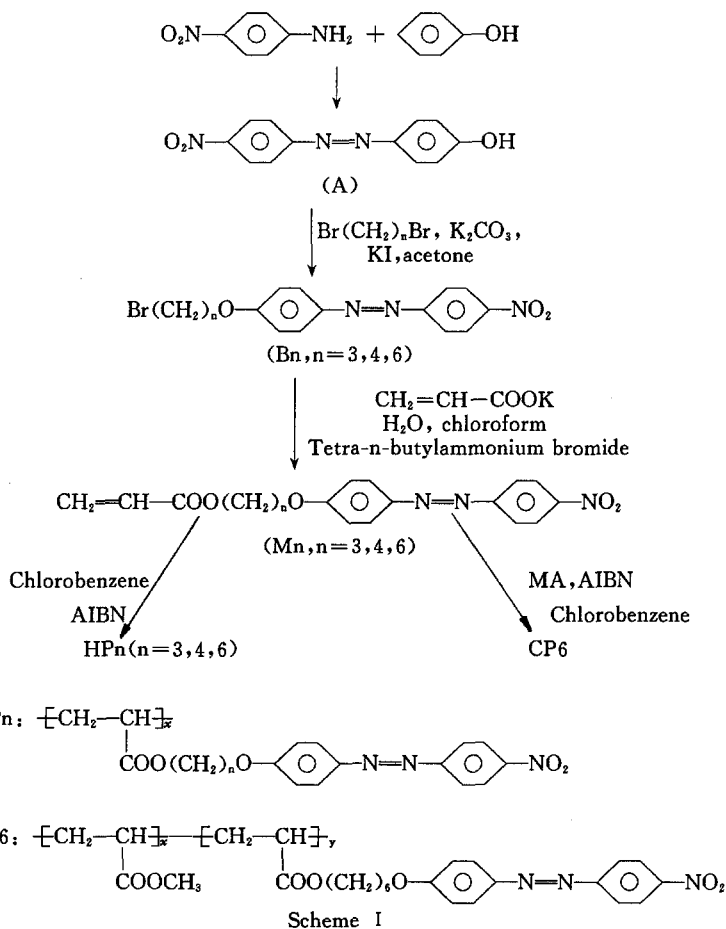
Side chain liquid crystalline polymers have attracted more attention and have been the subject of the extensive investigation in recent years(1) because of their application potential in electrooptic technologies and the fundamental importance of this class of materials. Their application potential based on the duality exhibited by the side chain liquid crystalline polymers, combining the properties of macromolecules, such as glass-transition property which makes the liquid crystalline orientation frozen-in, and the electrooptical properties of the low-molar-mass mesogens (2). It's highly promising for side chain liquid crystalline polymers to be used in information storage and nonlinear optics.

We synthesized polyacrylates containing para-nitro azobenzene which has a positive dielectric anisotropy( $\Delta\epsilon$ ) and high permanent dipolar moment (4.2D). This kind of polymers should possess high nonlinear optical effect because of the charge transfer property of mesogens which have highly delocalized  $\pi$  electron systems with attached electron donor and electron acceptor groups(3) and the methacrylate and acrylate polymers containing dipolar azo groups in the side chains have recently been demonstrated to have a large third-order (4) or second-order nonlinear optical effect (5). The present paper reported the SHG property of the polymer poled by corona-poling technique to obtain the noncentrosymmetric structure for satisfying the symmetric requirement of the second order nonlinear optical materials studied by UV-visible spectra and Maker-fringer measurement. The results showed this kind of polymer may be used as NLO materials.

\* Present address: Department of Material Science, Jilin University, Changchun 130023, People's Republic of China

## Experimental

The synthesis route taken to prepare the polymers is given in scheme I



4-hydroxy-4'-nitroazobenzene, A

The coupling of a diazotized aniline with phenol is described in detail elsewhere (6).

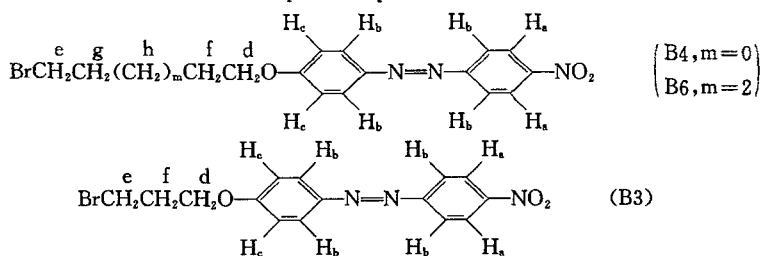
1-Bromo-*n*-(4-nitroazobenzene-4'-oxy)alkane, Bn ( $n=3, 4, 6$ )

Bn was synthesized according to typical procedure (7); 4-hydroxy-4'-nitroazobenzene (0.01 mol), 1,*n*-dibromoalkane (0.1 mol), potassium carbonate (10g, 0.072 mol), and potassium iodide (0.1g,  $6 \times 10^{-4}$  mol) in acetone (40 mL) were refluxed for 24h. After cooling to room temperature, the reaction mixture was filtered to remove the inorganic salts. Acetone was eliminated from the filtrate after distillation. The waxy residue was diluted with hexane (100 mL), and the resulting solution was cooled to  $-18^\circ\text{C}$  for a few hours. The precipitate was filtered off, washed with cold hexane, and then recrystallized twice from ethanol to ensure complete removal of any dimeric by-products that may have formed during the reaction.

IR (KBr):  $\nu=2938, 2953\text{cm}^{-1}$  vs  $(\text{CH}_2)$ ;  $1602, 1578, 1497\text{cm}^{-1}$ , aromatic ring stretch;  $1520, 1342\text{cm}^{-1}$  vs  $(\text{NO}_2)$ , vs  $(\text{NO}_2)$ ;  $1250\text{cm}^{-1}$ , vs  $(\text{C}-\text{O}-\text{C})$ ;  $835, 859\text{cm}^{-1}$  vs  $(\text{C}-\text{N})$ ,  $\delta(\text{C}-\text{H})$ ;  $641\text{cm}^{-1}$  vs  $(\text{C}-\text{Br})$

$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) spectroscopic data of the Bn were given in Table 1

Table 1  $^1\text{H}$  NMR spectroscopic data for Bn ( $n=3,4,6$ )



Sample	$\delta$ (ppm)
B3	2.39(m, 2H, Hf), 3.65(t, 2H, He) 4.22(t, 2H, Hd), 7.02(m, 2H, Hc), 7.97(m, 4H, Hb) 8.37(m, 2H, Ha)
B4	2.05(m, 2H, Hg), 2.12(m, 2H, Hf), 3.54(t, 2H, He) 4.12(t, 2H, Hd), 7.02(m, 2H, Hc), 7.97(m, 4H, Hb) 8.37(m, 2H, Ha)
B6	1.52(quin, 4H, Hh), 1.71(quin, 2H, Hg), 1.93(quin, 2H, Hf) 3.45(t, 2H, He), 4.07(t, 2H, Hd), 7.02(m, 2H, Hc) 7.97(m, 4H, Hb), 8.37(m, 2H, Ha)

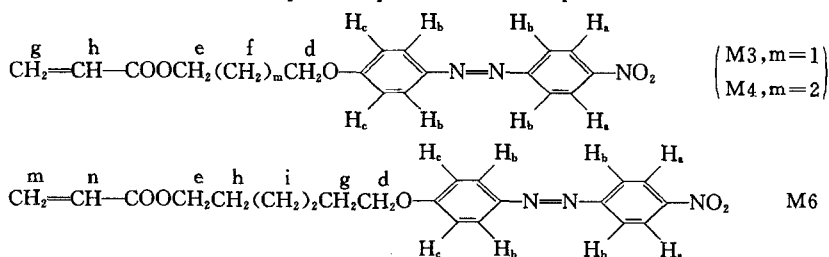
1-[4-nitroazobenzene-4'-oxy] alkyl acrylates ( $M_n$ ,  $n=3,4,6$ )

The acrylates,  $M_n$  were synthesized by liquid-liquid phase-transfer catalysis reaction between Bn and potassium acrylate using tetrabutylammonium bromide as phase transfer catalyst. Typical procedure is; A mixture of Bn (0.01 mol), tetrabutylammonium bromide (0.001 mol) in 50 mL of chloroform, and 100 mL (0.1 mol) of potassium acrylate solution was refluxed for 96h. The compounds  $M_n$  were extracted from the reaction mixture with chloroform, washed with water, and dried over sodium sulfate. The solvent (chloroform) was evaporated and the solution was precipitated by adding a large excess of methanol, the precipitate was filtered off, dried under vacuum for 24hr. at  $50^\circ\text{C}$ .

IR(KBr): 2938, 2868  $\text{cm}^{-1}$  vs ( $\text{CH}_2$ ); 1719  $\text{cm}^{-1}$  vs ( $\text{C}=\text{O}$ ); 1640  $\text{cm}^{-1}$  vs ( $\text{C}=\text{C}$ ); 1600, 1580, 1495  $\text{cm}^{-1}$ , aromatic ring stretch; 1520, 1342  $\text{cm}^{-1}$  vs ( $\text{NO}_2$ ), vs ( $\text{NO}_2$ ); 1250  $\text{cm}^{-1}$  vs ( $\text{C}-\text{O}-\text{C}$ ); 835, 859  $\text{cm}^{-1}$  vs ( $\text{C}-\text{N}$ ),  $\delta$ ( $\text{C}-\text{H}$ ).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectroscopic data of the compounds  $M_n$  were given in Table 2

Table 2  $^1\text{H}$  NMR spectroscopic data of the compounds  $M_n$



Sample	$\delta$ (ppm)
M3	2. 21(m, 2H, Hf), 4. 20(t, 2H, Hd), 4. 41(t, 2H, He), 6. 5~5. 7(m, 3H, Hg, Hh), 7. 06(m, 2H, Hc), 8. 00(m, 4H, Hb), 8. 37(m, 2H, Ha)
M4	1. 95(m, 4H, Hf), 4. 10(t, 2H, Hd), 4. 27(t, 2H, He), 6. 5~5. 7(m, 3H, Hg, Hh), 7. 06(m, 2H, Hc), 8. 00(m, 4H, Hb), 8. 37(m, 2H, Ha)
M6	1. 5(m, 4H, Hi), 1. 7(m, 2H, Hg), 1. 8(m, 2H, Hh), 4. 07(t, 2H, Hd) 4. 18(t, 2H, He), 7. 06(m, 2H, Ha), 8. 00(m, 4H, Hb), 8. 37(m, 2H, Ha)

### Polymers HPn and copolymers CP6

Compounds Mn were radically polymerized in chlorobenzene solution using AIBN as initiator under nitrogen at 80°C for 48h. The resultant polymer solution was precipitated by methanol to give HPn which was washed twice by hot ethanol, dried under vacuum at 30°C for 24h.

IR(KBr): 2935, 2853, 1728, 1601, 1580, 1497, 1520, 1340, 1250, 835, 859  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR spectrum of HP6 was given in Fig. 1a. It can be seen that peak around 5.7~6.3 ppm attributed to the proton of  $\text{CH}_2=\text{CH}-$  disappeared, whereas there appeared a peak around 2.3 ppm which was attributed to the proton of methylene groups of the polymer backbone.

M6 and methyl acrylate were copolymerized in chlorobenzene to give CP6. The experimental details were the same as that of HPn.

$^1\text{H}$  NMR spectrum of CP6 was given in Fig. 1b. The attribution of the peaks was also given in Fig. 1b. The molar ratio of MA and M6 in the copolymers were determined by cut-paper weighting method of  $^1\text{H}$  NMR spectra.

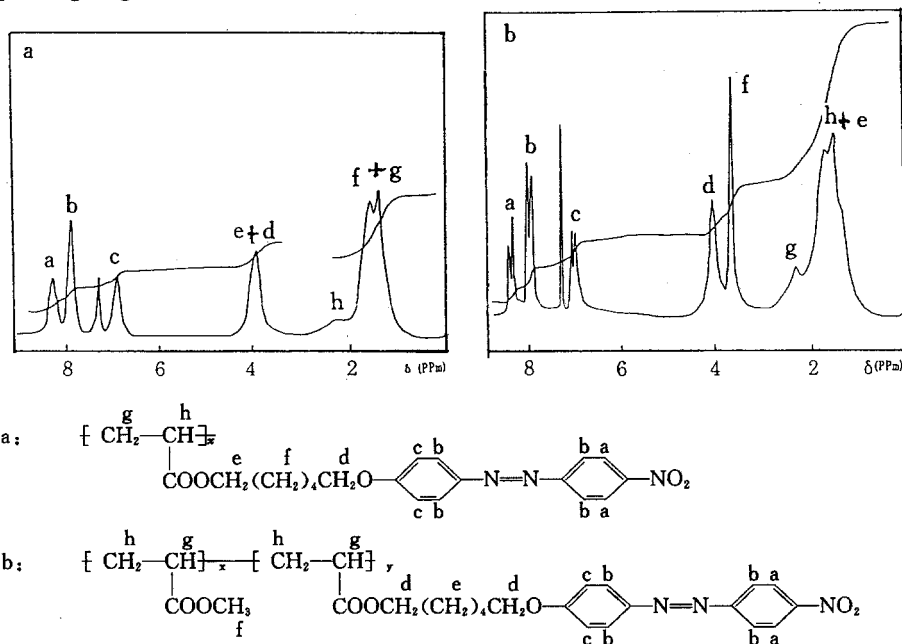


Fig. 1  $^1\text{H}$  NMR spectra of HP6 (a) and CP6 with  $x/y=50/50$ (b)

### Corona poling

In order to study the second-order nonlinear optical property of the polymers, corona poling technique was used to orient the mesogens. A solution of HP6 in chloroform was spin-coated

at 800 rpm onto a 1 mm-thick transparent glass plate with ITO on it followed by a bake at 30°C for 24h. to remove the residual solvent. The glass plate was placed film — side — up onto a ground planar aluminum electrode, a needle electrode was placed 1cm above the ground planar aluminum electrode. Raising the temperature of the film to a certain temperature, a high positive voltage was applied to the suspended electrode. After a period of poling, while the voltage was held constant, the temperature of the film was lowered below  $T_g$ . The poled film showed more transparent than the unpoled film.

#### Measurement

The proposed molecular structure for the compounds and polymers were verified by  $^1\text{H}$  NMR spectroscopy with a Varian Unity-400 MHz spectrometer in  $\text{CDCl}_3$ , by IR spectroscopy with a NICOLET 50X-FTIR spectrometer.

The thermal properties of the polymers were investigated with a Perkin-Elmer DSC-2 differential scanning calorimeter. The heating rate was  $10\text{K} \cdot \text{min}^{-1}$  except for special notation.

The optical studies were performed with a Zeiss-Jena polarizing optical microscope equipped with a hot stage.

The WAXD were recorded on philips PW1700 automatic powder diffractometer.

The UV-visible spectra of the poled and unpoled polymer films were recorded on Ziess VU<sub>2</sub>-P UV-visible spectrometer.

#### Results and discussion

##### Phase behaviour of the polymers

The thermal properties of the homopolymers (HPn) were studied by DSC and POM. The transitional properties of HPn are listed in Table 3

Table 3 Transitional properties of HPn

HPn	$T_g$ (K)	$T_m$ (K)	$T_{NI}$ (K)
n=3	318.7	324.3	—
n=4	309.8	340.6	—
n=6	308.9	341.4	401

It can be seen that  $T_g$  decreased with increasing the length of the spacer. According to Gibbs and Dimarzio (8), the essence of the glass transition of the polymers is a conformational rearrangement process. The influence of the length of the spacer on  $T_g$  of the side chain polymers lies in the following two aspects; [1] the volume of the side groups increased with increasing length of the spacer, which results in the rotational energy of the segment increasing, so  $T_g$  increased; [2] the hinder of the rigid mesogen to the rotation of the polymer backbone decreased with increasing length of spacer, so  $T_g$  decreased. Considering the two opposite effect of the spacer on  $T_g$ , we thought that the factor [2] was dominant for short spacers, but for long spacers, factor [1] was dominant. When n changed from 3 to 4,  $T_g$  decreased 8K, but for n from 4 to 6,  $T_g$  decreased only 1K.

The influence of the length of the spacer on  $T_m$  reflected the different crystallinity of the polymers with different length of spacer. Fig. 2 is WAXD of HPn. The relative intensity of the amorphous diffraction peak increased, while that of the crystalline diffraction peak decreased with decreasing n. According to results of WAXD of HPn, the crystallinity increased with n. Results of WAXD and DSC indicated that the regularity of the arrangement of the mesogens increased with increasing n.

No liquid crystalline endotherm could be observed even after repeated thermal cycles and annealing for HP3 and HP4. It's only with HP6 having six carbons in the spacer, that the liq-

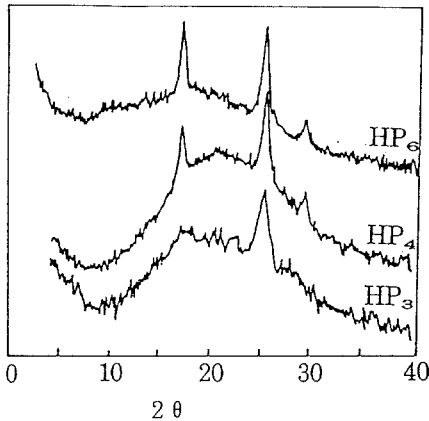


Fig. 2 WAXD spectra of HPn at room temperature

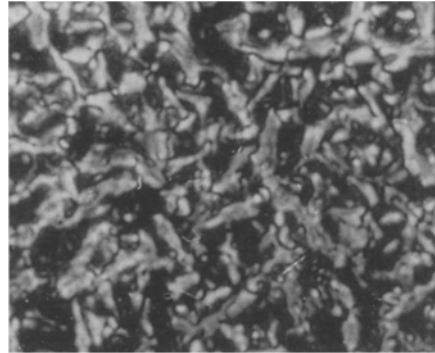


Fig. 3 POM photograph of HP6 annealed at 363K for 2 hr. ( $\times 600$ )

uid crystalline property could be observed. The DSC curve of HP6 was given in Fig. 4. The three transition corresponded to  $T_g$ ,  $T_m$  and  $T_{NI}$  respectively. The optical texture of HP6 in its LC state which was annealed at 363K for 2hr. was given in Fig. 3. The typical schlieren texture showing nematic phase was observed. and its nematic liquid crystalline behaviour was also confirmed by WAXD, in which there was a diffuse peak around  $2\theta = 20^\circ$ , indicating that one-dimensional order existed in the LC phase of HP6.

The influence of the noncrystalline comonomer (MA) on the properties of the polymers was studied by DSC and WAXD. Fig. 4 were the DSC curves of CP6 with different molar content of MA. Notice that  $T_g$  decreased linearly with increasing the molar content of MA in CP6.

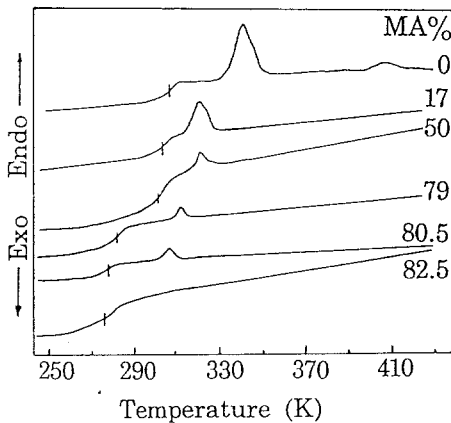


Fig. 4 DSC curves of HP6 and CP6 with different molar content of MA

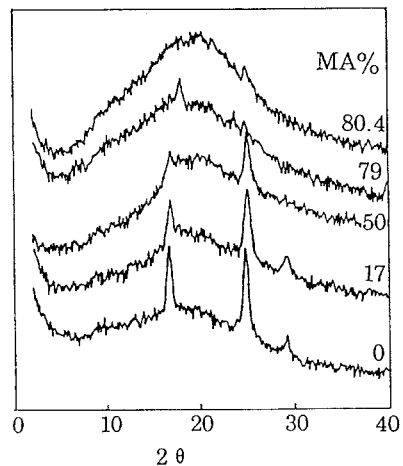


Fig. 5 WAXD spectra of CP6 with different molar content of MA

The tendency of  $T_g$  versus MA concentration was accordance with that of Gordon-Taylor (9) equation which could be applied to random copolymers. Another effect of non-crystalline component MA on the transitional properties of MA was that on crystallinity.  $T_m$  and  $\Delta H_m$  of the copolymers CP6 decreased with increasing MA content. WAXD spectra of CP6 were given

in Fig. 5. The three diffraction peaks were  $d_1 = 0.52$  nm,  $d_2 = 0.35$  nm, and  $d_3 = 0.30$  nm, which were similar to that of the homopolymers. Increasing MA content in the copolymers, the relative intensity of the diffraction peaks decreased while that of the amorphous diffuse peaks increased.

Results of WAXD of CP6 indicated that introduction of amorphous MA reduced the crystallinity of CP6,  $T_m$  and  $\Delta H_m$  decreased with increasing MA content.

From the DSC curves of CP6, it can be seen that no liquid crystallinity could be observed for the copolymers in which molar content of MA was larger than 17%.

The above studies showed that length of spacer and the composition of the copolymer had the influence on the  $T_g$ ,  $T_m$  as well as the liquid crystallinity.

#### *Nonlinear optical property of the polymer.*

In order to be used in second order nonlinear optics, materials must possess noncentrosymmetric structures. In our experiments, corona poling technique was used to orient the chromophore to eliminate the symmetric center. Fig. 6 shows the spectra of the poled and unpoled polymer films of HP6. For poled films, a decrease in absorbance (hypochromic shift) were observed. It is well known that during poling a surface charge accumulates at the surface of the polymer film with opposite charges at the planer electrode (10), thus a large electrostatic field is created and interacts with the chromophores and alters the absorption spectrum. The electrostatic field orients the dipoles in the direction of the electric field, which lead to a change in the intensity of the absorption spectrum. Also, a large electrostatic field can induce a change in the dipole moment of the molecules and makes bathochromic shift. For the polymer HP6, the bathochromic shift was only 2–3nm, because of the chromophores were attached to the polymer backbone covalently.

UV – visible spectroscopic study on the poled HP6 film showed that corona poling was effective to orient the mesogens of this kind of polymers. By using the formula  $\Phi = 1 - A_{\perp} / A_0$ , where  $A_{\perp}$  is the absorbance of a poled polymer with electric field polarized perpendicular to the poling direction and  $A_0$  is the absorbance of the unpoled polymer film. The order parameter of the above poled HP6 was 0.41.

Maker-fringer method was used to study the second-harmonic generation (SHG) property of the poled HP6 film. When the thickness of the poled HP6 film (poling conditions: 11kV 358K, 30min.) was less than 1  $\mu\text{m}$  and the output of the laser was less than 1m J, the output SHG signal was 3.4V (debating the noise signal). The SHG signal of the poled film was detected experimentally, which suggested that this kind of polymers possessed second-order nonlinear optical properties. Some quantitative measurements of  $\chi^{(2)}$  were in progress.

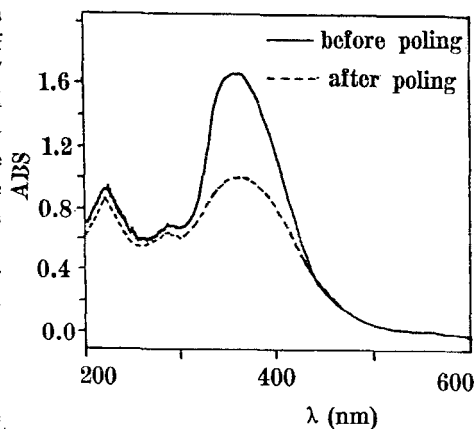


Fig. 6 UV – visible spectra of poled and unpoled HP6 films  
poling, 11kV, 358K, 30min.

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