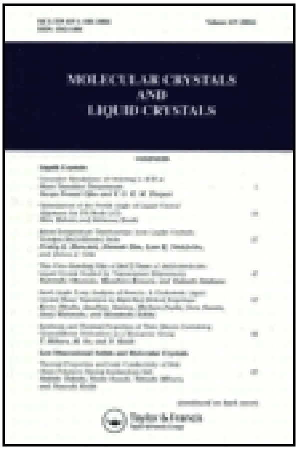

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Nonlinear Optical Active Polymethacrylates with High Glass Transition Temperatures

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NONLINEAR OPTICAL ACTIVE POLYMETHACRYLATES WITH HIGH GLASS TRANSITION TEMPERATURES

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Abstract Chromophore relaxation is still one of the major problems with NLO polymers. One strategy to overcome this problem is the synthesis of polymers with high glass transition temperatures. We have prepared a number of polymers by copolymerization of NLO-active methacrylates with the bulky adamantyl methacrylate. This leads to polymers with glass transition temperatures up to 190 °C. The synthesis and properties of these polymers are reported in detail. The polymers show a good long term stability of the electrooptic coefficient (r_{33}) at elevated temperatures. So polymer **3c** with a bisazo chromophore shows only a 25 % EO-coefficient decay after one month at 120 °C.

INTRODUCTION

To be suitable for device applications, electrooptic (EO) polymers must exhibit large EO-coefficients and a sufficient stability of chromophore orientation. To realize these basic requirements in one material causes some problems. Large EO-coefficients require large amounts of chromophores with sufficient nonlinearities. These chromophores must endure the poling procedure at high temperatures and therefore be sufficiently thermally stable. Furthermore stability of chromophore orientation strongly depends on the glass transition temperature of the material which is in general reduced by a large chromophore content in the polymer. So one has to find a compromise in combining the fundamental properties mentioned above. Finally for any application of electrooptic polymers in devices good film forming properties, low optical losses in the near infrared and a possibility for waveguide formation are required. The critical point is that a polymer must fulfill all these specifications at the same time. Otherwise it becomes useless for technical applications.

In recent years much progress has been made in synthesis of chromophores with large nonlinear optical responses and sufficient thermal stability. In this context chromophores based on heteroaromatics, in many cases thiophene groups, are of special interest because of their large molecular nonlinearities[1,2).

For side group polymers with the NLO chromophores covalently attached to the backbone high EO-coefficients of up to 40 pm/V have been reported$^{3)}$. Unfortunately, the chromophore orientation obtained by poling of such materials is often not stable resulting in a slow decay of the electrooptic coefficient.

There are two strategies to overcome the problem of chromophore relaxation. One of them is crosslinking after poling. A second way to enhance the stability of chromophore orientation is the use of polymers with high glass transition temperatures. In this paper we report on NLO-active polymethacrylates with high glass transition temperatures. We have synthesized copolymers of adamantyl methacrylate and some NLO-active methacrylates by free radical polymerization. The bulky adamantyl side groups strongly hinder the backbone mobility leading to glass transition temperatures between 160 and 200 °C depending on the chromophore content.

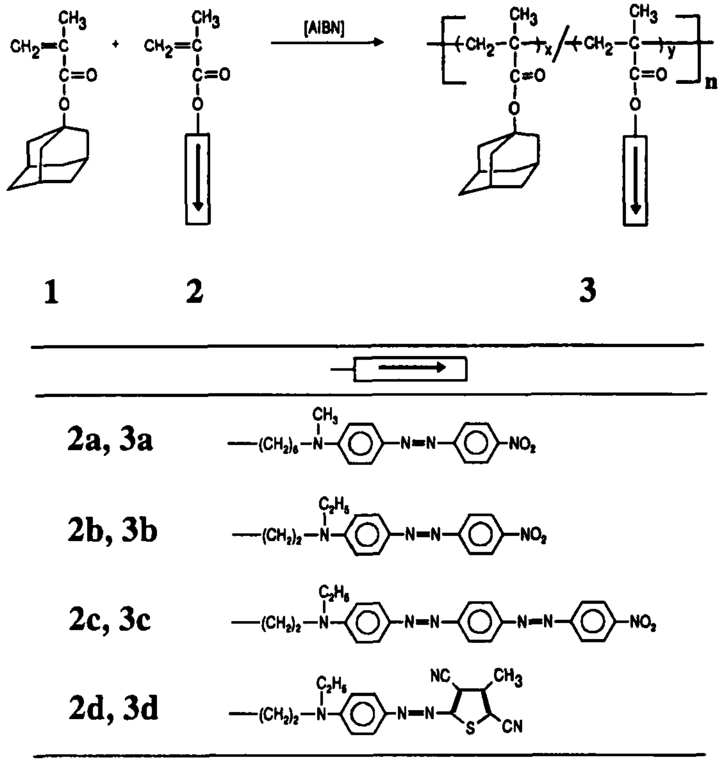
RESULTS AND DISCUSSION

For reasons of poling efficiency NLO-active polymethacrylates are in general copolymers of NLO-active methacrylates and commercial methacrylates as comonomers. We have reported that only comonomers with very bulky substituents lead to polymethacrylates with glass transitions up to 200 °C$^{4,5)}$ which are necessary for a real progress in the long term stability of chromophore orientation$^{6)}$. 1-Adamantyl methacrylate (AdMA) is such a comonomer. Its homopolymer Poly(1-adamantyl methacrylate) P(AdMA) exhibits a T_G of above 230 °C and for copolymers of AdMA and MMA glass transition temperatures between 125 and 230 °C depending on the mole fraction of AdMA have been reported$^{7)}$.

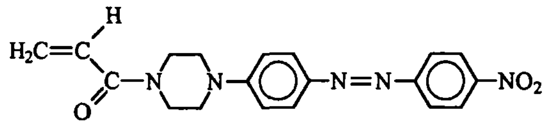
We synthesized a number of copolymers of AdMA **1** and the NLO-active methacrylates **2a-d** shown in scheme 1. Beside the well known azo chromophores **2a** and **b**, the bisazo dye **2c** and the azo dye **2d** with a thiophene group as electron acceptor have been used. All polymethacrylates **3a-d** were prepared by free radical polymerization in chlorobenzene with AIBN as initiator. Some typical results of these polymerizations are presented in table 1. Detailed information about the polymerization conditions, molecular weights and copolymerization parameters is provided in references 4 and 5.

Except **3a** all polymers exhibit remarkably high glass transition temperatures in the range of 170 to 190 °C (see table 1). In general, glass transition temperatures of our NLO-active polymethacrylates decrease with increasing chromophore content in the polymer since the chromophores act as plasticizers. To get an idea of this decrease and to find a good balance between high chromophore loadings and high glass transition temperatures we have prepared three series of copolymers with the chromophores **2a**, **b** and **d** and varying monomer ratios in feed. The results of these series are plotted in figure 1. Figure 1 gives evidence for the strong influence of the spacer length on the glass transition temperature. Polymers **3a** with a long flexible spacer of six methylene units show a drastic decrease of T_G with increasing chromophore content. For example a polymer with 34 mole % of **2a** exhibits a glass transition of only 118 °C. If chromophores with short spacers of two methylene units are used (polymers **3b** and **d**) the decrease of T_G is much less pronounced. Polymer **3b** with an analogous chromophore content of 34 mole % undergoes a glass transition at 170 °C and polymer **3d** with 38 mole % at 179 °C. So copolymerization of AdMA **1** and NLO-active methacrylates with short spacers of two methylene units allows the synthesis of polymethacrylates possessing both high chromophore loadings and high glass transition temperatures.

SCHEME 1:



Please note that the glass transition temperatures of our polymethacrylates with chromophore contents above 30 mole % range between 165 and 180 °C. As will be shown at the end of the paper these polymers already possess good long term stabilities of the electrooptic coefficient but the stabilities are still too low for applications at elevated temperatures. So we now try to synthesize polymethacrylates with glass transition temperatures of 200 to 220 °C. Recently we have tested the modified Disperse Red chromophore 4 with piperazine as spacer.



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Compared to common alkyl spacers the piperazine group should cause additional hindering of the backbone mobility and therefore create even higher TGs. Although

TABLE 1: Synthesis of the NLO-active polymethacrylates **3a-d** a)

Poly-mer	Monomer ratio in feed mole-%		Mole ratio in polymer b) mole-%		Yield %	Molecular weight c) $10^{-3} M_w$	$10^{-3} M_n$	M_w/M_n	T_G d) °C
3a	0.60	0.40	0.66	0.34	41	109	42	2.6	118
3b	0.60	0.40	0.61	0.39	73	229	126	1.8	168
3c	0.70	0.30	0.76	0.24	50	96	12	- e)	186
3d	0.70	0.30	0.73	0.27	85	125	36	3.4	184
3d	0.60	0.40	0.62	0.38	84	86	30	2.9	179

a) All polymers were prepared by free radical polymerization in chlorobenzene solution. For experimental details see reference 4).

b) Determined by ^{1}H-NMR spectroscopy.

c) Determined by gel-permeation chromatography with polystyrene standards, solvent: tetradydrofuran with 0.25 % of tetrabutylammonium bromide.

d) Glass transition temperature determined by DSC, heating rate 10 K/min

e) Bimodal molecular weight distribution

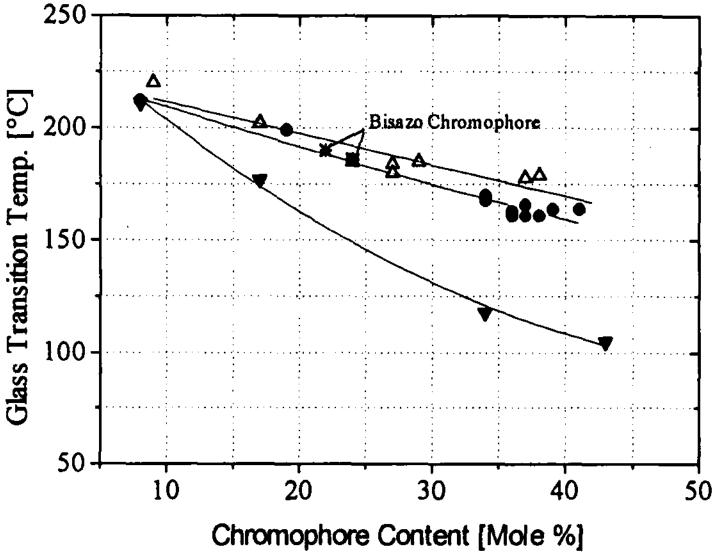

FIGURE 1: Dependence of the glass transition temperature on the contents of NLO chromophores in the polymethacrylates: **3a** (▼), **3b** (●), **3c** (✱) and **3d** (Δ)

acrylates in general have lower glass transition temperatures than comparable methacrylates we have used the acrylate monomer since the corresponding methacrylate did not show any polymerization tendency when copolymerized with AdMA or in homopolymerization. This is in agreement with results reported in literature some years ago[8,9]. Nevertheless copolymerization of AdMA **1** with the NLO chromophore **4** results in polymers exhibiting T_Gs of almost 200 °C. For example a polymer with 33 mole % of chromophore **4** exhibits a glass transition temperature of 197 °C. This is a further progress towards the goal of high glass transition temperatures followed by sufficient stabilities of chromophore orientation at elevated temperatures.

The electrooptic properties of polymers **3b** and **3d** have been reported in detail elsewhere[4,10]. Additional measurements on the long term stability of the electrooptic coefficient r_{33} up to 8 months were carried out recently and are presented in figure 2.

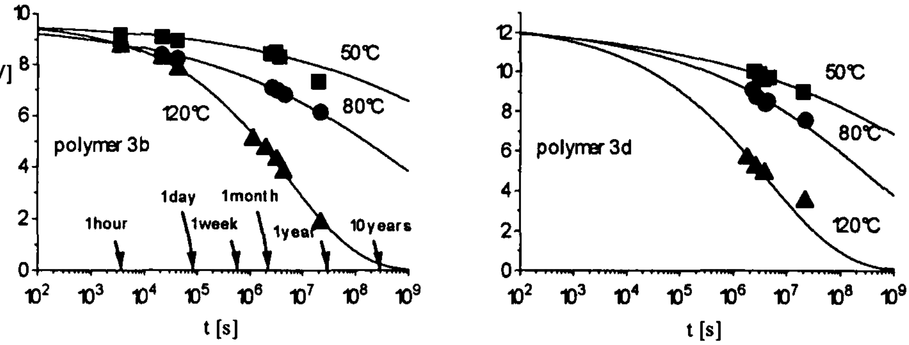

FIGURE 2: Long term relaxation of the electrooptic coefficient r_{33} (at 1541 nm) for polymers **3b** and **d** at temperatures of 50, 80 and 120 °C. Solid curves represent KWW-fits to the experimental data. Poling field strength: 100 V/μm for both polymers.

Figure 2 shows the decay of the r_{33}-coefficient measured at 1541 nm as a function of time for the two polymers stored at 50, 80 and 120 °C. Chromophore contents and glass transition temperatures of both polymers are specified in table 1. The solid curves represent KWW-fits to the experimental data. The data points taken after 8 months have been added to the plots without changing the original KWW-fits. So it becomes evident from figure 2 that apart from small deviations the relaxation of the r_{33}-coefficient follows a KWW-function. Long term stability of the EO-coefficient is quite similar for both polymers. After 8 months polymer **3b** with Disperse Red side groups shows 77 %, 66 % and 20 % of the initial EO-coefficients at 50 °C, 80 °C and 120 °C, respectively. The corresponding values for polymer **3d** with thiophene side groups are 75 %, 63 % and 29 %.

Corresponding stability measurements for polymer **3c** with the bisazo chromophore are plotted in figure 3. The sample has a chromophore content of 22 mole % of **2c** and undergoes a glass transition at 190 °C. Its low r_{33}-coefficient is due to the low poling field of 60 V/μm and the chromophore content of 22 mole %. Stability measurements were carried out at 120 and 140 °C since at lower temperatures no significant decay of the r_{33}-coefficient could be observed. Polymer **3c** is the most stable one in the whole series. So far it is not clear whether this high stability is a consequence of the higher glass transition temperature of the material or of the rod-like shape of chromophore **2c** which limits its mobility. To examine this problem stability measurements with polymers **3b** and comparable glass transition temperatures of about 190 °C will be carried out in the near future.

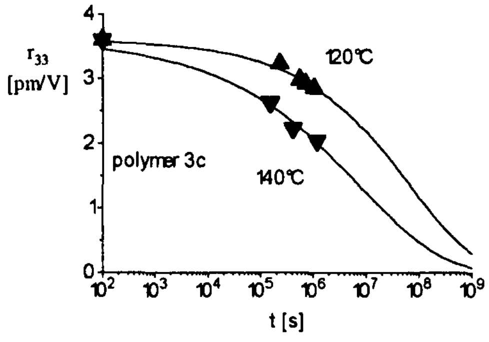

FIGURE 3: Relaxation of the electrooptic coefficient r_{33} (1541 nm) for polymer **3c** at temperatures of 120 and 140 °C. Solid curves represent KWW-fits to the experimental data. Poling field strength: 60 V/μm.

CONCLUSIONS

The novel polymethacrylates presented in this paper exhibit glass transitions in the range from 165 - 200 °C. EO-coefficients r_{33} of up to 12 pm/V have been measured after poling with 100 V/μm. We expect that these values can be further enhanced by increasing the poling voltage. Due to their high T_G the polymers show remarkable EO-coefficient stability at elevated temperatures. Polymer **3c** with a bisazo chromophore shows only a 25 % EO-coefficient decay after one month of storage at 120 °C. From polymer **3b** channeled waveguides with optical losses of 1 dB/cm have been fabricated by selective ion etching[10]. So these easily processible materials are good candidates to fulfill the complex requirements for applicable NLO-materials in the future.

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