Preparation of Polysiloxane with Pendant Cr-bound Carbazole Chromophore for Nonlinear Optics

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ABSTRACT: A novel η^6-complex of *N*-allylcarbazole containing chromium tricarbonyl was synthesized. This complex was hydrosilylated with polymethylhydrosiloxane to afford a substituted polymer. Both the complex and the polymer were characterized by classical spectroscopy techniques (FTIR, NMR, and UV–vis), gel permeation chromatography, elemental analysis, and thermal analysis (TGA and DSC). The glass transition temperature of the polymer was found to be above 100°C and its thermal decomposition temperature was above 280°C. The polymer was amorphous in nature and formed excellent homogeneous films of good optical transparency. The third nonlinear optical properties of this polymer film coated on quartz substrate were studied by time-resolved forward degenerate four-wave mixing (DFWM). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 4076–4081, 2008

Key words: hydrosilylation; nonlinear optics; degenerate four-wave mixing; chromium tricarbonyl

INTRODUCTION

Carbazole-containing polymers as a kind of well-known photoconductive polymer have been widely used as host polymers in host-guest photorefractive and optoelectronic polymer composites.[1] We have previously reported an organometallic push-pull polymer in which the Cr(CO)₃ group is coordinated with the carbazole unit. This Cr-bound carbazole polymer features low-energy metal to ligand charge-transfer (MLCT) excited states that exert a considerable influence on its nonlinear optical (NLO) properties.[2] The Cr(CO)₃ group functions as either an effective ground-state acceptor or an excited-state donor, a characteristic not found in usual organic substitutions. It leads to a highly nonlinear molecular structure with a modest ground-state dipole moment.[3,4] In sharp contrast, in conventional donor/acceptor aromatic systems, a highly nonlinear molecular structure usually has a large dipole moment.[5–7]

The incorporation of organometallic groups into these polymers, however, made them a stiff, brittle material with a high glass transition temperature (T_g). The high T_g of these organometallic polymers normally requires high processing temperatures that can cause significant polymer degradations. In addition, it is very difficult to prepare films from these high T_g polymers, and therefore limits their possible applications in optoelectronic devices. Low T_g carbazole-containing polymers could be synthesized by incorporating carbazole unit into low T_g polymers. In particular, if carbazole units are incorporated into polysilane as reported by Tieke and Chard,[8,9] it is expected that these polymers would be able to maintain some carbazole chromophore relevant properties.

To find a better nonlinear optical material with improved mechanical processed-ability and film-forming properties, we synthesized a new organometallic polymer polymethylhydrosiloxane (N-allyl-carbazole)Cr(CO)₃ **PSX-ACzC** (Scheme 1) in which (*N*-allylcarbazole)Cr(CO)₃ **ACzC** were pendant chromophores and polymethylhydrosiloxaneas was the main chain. The NLO properties of this new polymer have been examined by degenerate time-resolved forward four-wave mixing (DFWM).

EXPERIMENTAL

General procedures

Unless otherwise noted, all manipulations with air-sensitive materials were performed under a nitrogen atmosphere using standard Schlenk techniques and a Vacuum Atmospheres dry box. Solvents were freshly distilled over appropriate drying reagents, and all Schlenk flasks were flame-dried under vacuum prior to use. Cr(CO)₆ (99%; Strem Chemicals, USA) was sublimed prior to use. Polymethylhydrosiloxane(Aldrich, Steinhelm, Germany) was used as

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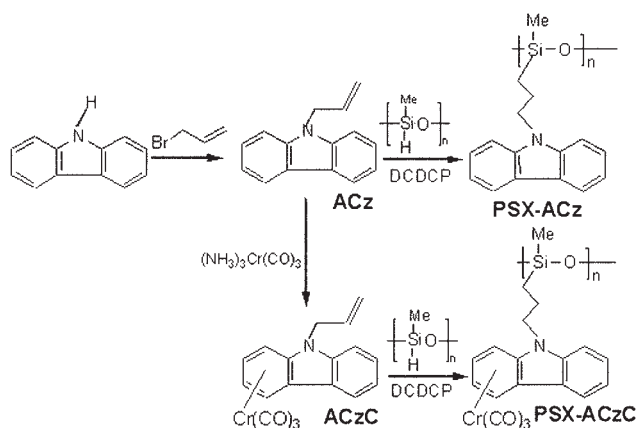
Scheme 1 Preparation of polymer PSX-ACz and PSX-ACzC.

received. Carbazole (98%, Aldrich) was used as received. N-allylcarbazole was synthesized with the method of Hopfinger[10] and dicyclopentadienedichloroplatinum (DCDCP) was synthesized with the method of Doyle.[11] Melting points were measured using a Reichert Thermopan melting point microscope. NMR spectra were recorded on a Bruker AVANCE 500 spectrometer. Chemical shifts are referenced in ppm to internal Me_4Si for the ^1H and ^{13}C NMR spectra. IR spectra were recorded on a cNicolet Magna-IR 550 instrument in KBr pellets. Elemental analyses were carried out on an Elementar Vario EL III analyzer (C, H and N) and TJARIS 1000 instrument (Cr). Electron-impact mass spectra were recorded on a Micromass GCT (EI, 70 eV) mass spectrometer. Molecular weight measurements were carried out in a PE Series 200 gel permeation chromatograph (GPC) with polystyrene as the standard, using THF as the eluent (30°C) at a flow rate of 1 mL/min. Thermogravimetric analyses (TGA) were carried out using a TGA SDTA 851^e instruments with a heating rate of 10°C/min in a nitrogen flow (20 mL/min). The DSC-200 PC of TA instruments were used to measure the glass transition temperature (T_g) of the samples under nitrogen at a heating rate of 10°C/min from −5 to 300°C. UV–vis spectra were obtained on a Varian Cary 500 spectrophotometer and built by OLIS to incorporate computer control.

Synthesis of N-allylcarbazole Cr(CO)₃ ACzC

$Cr(CO)_6$ was reacted to give $(NH_3)_3Cr(CO)_3$ according to a literature method.[12] A mixture of 10.3 g (55.0 mmol) of $(NH_3)_3Cr(CO)_3$ and 3.1 g (15.5 mmol) of N-allylcarbazole was heated under reflux in 200 mL of dioxane for 5 h. After being cooled, the solution was filtered through a celite filter and the residue was washed with CH_2Cl_2 (2 × 10 mL). The combined filtrates were concentrated in vacuum to a

viscous orange residue. The crude product was transferred to a 5 × 35 cm silica gel column and chromatographed with hexane until all of the N-allylcarbazole excess had been eluted. The product was recrystallized from CH_2Cl_2/n-hexane mixtures to give the desired product as orange crystals. Yield: 2.56 g (48.2%); m.p.: 127°C. Anal. Calc. For $C_{18}H_{13}NO_3Cr$: C, 62.97; H, 3.82; N, 4.08; Cr,15.15; Found: C, 62.78; H, 3.84; N, 4.05; Cr, 15.21. ^1H NMR (CDCl$_3$, 500 MHz): δ = 4.72 (m, 2 H), δ = 5.10 (t, J = 12.2 Hz, 1 H), δ = 5.29 (dd, J = 10.1 Hz, J = 17.2 Hz, 2 H), δ = 5.58 (t, J = 12.4 Hz, 1 H), δ = 5.86 (d, J = 6.8 Hz, 1 H), δ = 6.12 (m, 1 H), δ = 6.61 (d, J = 6.3 Hz, 1 H), δ = 7.34 (m, 2 H), δ = 7.50 (t, J = 14.9 Hz, 1 H), δ = 7.92 (d, J = 7.6 Hz, 1 H), ^{13}C NMR (C$_6$D6, 125 MHz): δ: 45.94, 74.87, 85.36, 88.46, 92.35, 92.58, 109.80, 118.28, 120.09, 121.13, 122.45, 123.07, 127.68, 131.47, 142.61, 233.92. MS-EI (70 eV, m/z (%)): 343 (M$^+$, 14), 315 (M$^+$ - CO, 4), 287 (M$^+$ - 2CO, 13), 259 (M$^+$ - 3CO, 100), 207 (M$^+$ - Cr(CO)$_3$, 15), 52 (Cr$^+$, 49). IR (KBr): ν = 1954 and 1872 (C=O); 1612, 1551, 1470, 1437, 1055, 746 (carbazole).

Hydrosilylation reactions

The procedures for both hydrosilylation of N-allylcarbazole **ACz** and N-allylcarbazole CrC(CO)₃ **ACzC** were essentially the same. Here, taking **ACzC** for example. Hydrosilylation was carried out in freshly distilled toluene. Polymethylhydrosiloxane (Aldrich) was used as received. Dicyclopentadienedichloroplatinum (DCDCP) was used as the catalyzer. **ACzC** were freshly prepared before use. Fischer-Porter aerosol compatible tubes with valves were used for hydrosilylation reaction. A mixture of N-carbazole Cr(CO)₃ **ACzC** (3.4 g ,10 mmol), polymethylhydrosiloxane (0.4 g, 6.7 mmol), toluene (50 mL) and trace dicyclopentadienedichloroplatinum (DCDCP) were charged to the tubes; the tubes were sealed and degassed at 10^{-3} mm by three alternate freeze-thaw cycles. Liquid nitrogen was used as the freezing medium. After degassing, the tubes were placed in a thermostat for a predetermined amount of time at 65°C. After removal from the bath and cooled, the polymer was precipitated in rapidly swirling large excess of petroleum ether. When necessary, the polymer solution was diluted with more solvent before precipitation to obtain fine polymer particles rather than large chunks. This process was repeated three times to ensure that all monomers and other contaminants had been washed from the polymer. After precipitation the polymers were filtered and dried under high vacuum.

3 Yield: 1.67g (85.0%); Anal. Calc for **PSX-ACz**: C, 69.97; H, 6.32; O, 6.79; N, 5.05; Si, 11.87; Found: C, 69.82; H, 6.41; O, 6.77; N, 5.03; Si, 11.97. ^1H NMR (CD$_3$COCD$_3$, 500 MHz): δ (ppm): 8.1 (ArH), 7.0–7.4

(ArH), 4.0 (N—CH$_2$—), 1.7 (—CH$_2$—), 0.2 (—CH$_2$—Si), −0.2 (Si—CH$_3$). IR (KBr): ν = 1627, 1596, 1463, 748, 721 (carbazole); 1261, 844 (CH$_3$Si—O—); 1229 (C—N); 1002–1090 (Si—O—Si).

4 Yield: 2.59g (68.2%); Anal. Calc for **PSX-ACzC**: C, 54.24; H, 4.27; O, 16.61; N, 3.25; Si, 9.56; Cr, 12.07 Found: C, 54.31; H, 4.25; O, 16.58; N, 3.28; Si, 9.49; Cr, 12.09. ^{1}H NMR (CD$_3$COCD$_3$, 500 MHz): δ (ppm): 7.2–8.1 (ArH$_{(uncoord)}$), 5.2–6.9 (ArH$_{(coord)}$), 4.1 (N—CH$_2$—), 1.9 (—CH$_2$—), 0.6 (—CH$_2$Si), 0.1 (Si—CH$_3$). IR (KBr): ν = 1952, 1863 (CO); 1619, 1549, 1471, 748 (carbazole); 1263, 844 (CH3Si—O—); 1234 (C—N).

Polymer film preparation and NLO measurement

Polymethylhydrosiloxane *N*-allylcarbazole Cr(CO)$_3$ **PSX-ACzC** was dissolved in toluene and the solution (∼ 10 wt %) was filtered through syringe filters. Thin polymer films were spin-coated onto quartz substrate from this solution and dried in vacuum at 30°C for 24 h. The preparation of film **PSX-ACz** is the same as that of film **PSX-ACzC**.

The third-order NLO properties of the studied polymers were measured using the technique of time-resolved forward degenerate four-wave mixing (DFWM). The excitation source was a mode-locked Nd: YAG laser system (wavelength 532 nm, pulse width 35 ps, repetition rate 10 Hz, pulse energy 1.5 mJ). In the experiment, the intensity of the DFWM response for the film samples, corresponding to the maximum of temporal profiles obtained for a reference sample (CS$_2$ was employed in our case; its value was 6.8 × 10^{-13} esu at 532 nm) under the same light intensity conditions. The $\chi^{(3)}$ value and the nonlinear refractive index, n_2, of the samples were then calculated from eqs. (1) and (2), respectively.[13]

$$\chi^{(3)} = \left(\frac{I_4}{I_{4r}}\right)^{1/2}\frac{d_r}{d}\left(\frac{n}{n_r}\right)^2 \frac{\alpha d \exp\left(\alpha d/2\right)}{1 - \exp(-\alpha d)}\chi_r^3 \qquad (1)$$

$$n_2 = \frac{12\pi\chi^{(3)}}{n} \qquad (2)$$

There are various mechanisms, such as nonresonant instantaneous electronic polarization at the frequency of the driving fields, molecular reorientation caused by an anisotropy in the induced dipole moments, molecular libration, molecular redistribution, and electrostriction that contribute to the third-order optical nonlinearities of polymers, in which each mechanism corresponds to a characteristic respond time.[14,15] Due to its convenience for probing both magnitude of $\chi^{(3)}$ and its time response, DFWM plays an significant role in third-order nonlinear op-

tical studies, especially in polymer cases, for it serves us to distinguish the above mechanisms resulting in the change of $\chi^{(3)}$ by the analysis of time-resolved data.[14]

RESULTS AND DISCUSSION

Synthesis and characterization of compound ACzC, polymer PSX-ACz, and PSX-ACzC

Compound **ACzC** was synthesized according to a literature method,[16] which was an orange crystal and stable to atmospheric oxidation at low temperatures. The EI-mass spectrum of **ACzC** showed peaks of the highest mass that are consistent with its monomeric formula. The subsequent hydrosilylation reactions between allylic compounds (**ACz**, **ACzC**) and polymethylhydrosiloxane in the presence of DCDCP afforded substituted polymethylhydrosiloxanes (**PSX-ACz**, **PSX-ACzC**). The ^{1}H NMR and IR spectra of polymer **PSX-ACz** and **PSX-ACzC** showed the presence of functional groups of the corresponding parent molecules. Elemental analysis data confirmed that there was no loss of the metal unit from the pendant carbazole group in **PSX-ACzC**. Due to the presence of methyl groups at each Si center,[17] polymethylhydrosiloxane showed good solubility in many commonly used organic solvents. Consequently, the resulting polymer **PSX-ACz** was soluble in common solvents, such as chloroform and DMF. On the contrary, **PSX-ACzC** was only sparingly soluble in these solvents at room temperature while it was readily soluble in THF and toluene. Because of the good solubility in commonly used organic solvents, both **PSX-ACz** and **PSX-ACzC** can form thin homogeneous films of good optical quality by spin-coating on glass slides. Additionally, **PSX-ACzC** was found to be very stable toward air and moisture in its solid state and can be stored in solutions for an extended period of time without significant decomposition.

To assess the reactivity of **ACzC**, a total of eight hydrosilylation reactions were run with polymethylhydrosiloxane. The results are summarized in Table I. The percentage of chromium in the polymers as well as the polymer composition was determined by elemental analysis. As shown in Table I, the molar ratio of **ACzC** to polymethylhydrosiloxane has few effects on the yield of product whereas it affects significantly the hydrosilylation ratio. Prolonging the reaction time properly can increase both the yield of product and the ratio of hydrosilylation when the molar ratio of **ACzC** to polymethylhydrosiloxane is below 60 to 40. However, neither the molar ratio of **ACzC** to polymethylhydrosiloxane nor relaxation time has obvious effect if the molar ratio exceeds 60 to 40. For polymer **PSX-ACzC**, in comparison with protons (b in Fig. 1) in

TABLE I
Hydrosilylation Studies of (*N*-allylcarazole)Cr(CO)₃ with Polymethylhydro-siloxane at 70°C in Toluene

No.	M/P mole ratio	Time (hour)	Conversion (%)	Analysis (%Cr)	Ratio of hydrosilylation (mole-% M)	T_g (°C)
I	50/50	6	59.3	11.45	53.98	97
II	50/50	12	61.4	11.50	54.96	97
III	55/45	6	62.3	11.93	64.60	101
IV	55/45	12	65.6	12.11	69.45	102
V	60/40	6	67.7	12.75	92.53	108
VI	60/40	12	68.2	12.74	92.08	108
VII	70/30	6	68.1	12.74	92.08	107
VIII	70/30	12	68.0	12.73	91.63	107

uncoordinated ring, a significant upfield shift of protons (a in Fig. 1) in coordinated ring was found. This shift was anticipated, as the chromium tricarbonyl moiety lowers the bond order in the phenyl ring due to the electron withdraw.[18] The average molecular weight of **PSX-ACz** and **PSX-ACzC** were determined by gel permeation chromatography (GPC) using polystyrene standard as the reference. **PSX-ACz** showed an average molecular weight of M_n = 12,400 (DP is about 2.8), while **PSX-ACzC** had a lower average weight M_n = 9800 (DP is about 1.7). Clearly, Cr(CO)₃ group introduced to the carbazole unite exerts a significant influence on reactivity of the carbazole and the molecular weight characteristics of polymer obtained. The difference between **PSX-ACz** and **PSX-ACzC** is perhaps attributed the strong electron-withdrawing ability and steric bulkiness of Cr(CO)₃ fragment. The Cr(CO)₃ group is well known to stabilize both the benzylic carbanion and carbocation and apparently benzylic radical intermediates.[3,4] Thus, the η^6-Vinylarene-Cr(CO)₃ complex undergoes nucleophilic addition facilitated by stabilization of the benzylic carbanion with the Cr(CO)₃ moiety. The data obtained indicates that the incorporation of the Cr(CO)₃ group into *N*-vinylcarbazole results in the rearrangement of electron density of molecule and provides the probability of radical reactions with this

organometallic moiety.[16] For the system of **PSX-ACzC**, although the vinyl group is separated by one methyl group from the Cr-bound carbazole, the Cr(CO)₃ group is expected to have a noticeable stereo-electronic behavior which offers control of structure and property of organometallic polymer formed. On the other hand, mentioning that these polymers studied can be used to prepare high-quality films of the metallopolymers owing to the existence of polysilane chain. Cr-bound carbazole substitution on polymethylhydrosiloxane indictaes the orientation of polymer films on a molecular level, in addition the steric bulk of the Cr-bound carbazole subtituent defined by hydrosilylation controls the metallorganic polymer properties.

The thermal stability of both **PSX-ACz** and **PSX-ACzC** were carried out with thermal gravimetrical analysis (TGA) under nitrogen atmosphere. As shown in Figure 2, the decomposition of **PSX-ACzC** took place in two stages with maximum rates at 280 and 516°C, respectively, while **PSX-ACz** was decomposed only in one stage with a maximum rate at 510°C. The IR spectrum of **PSX-ACzC**, in which the sample was first heated to 290°C in nitrogen and then cooled down, showed no band assignable to the CO groups. It indicated that the initial weight
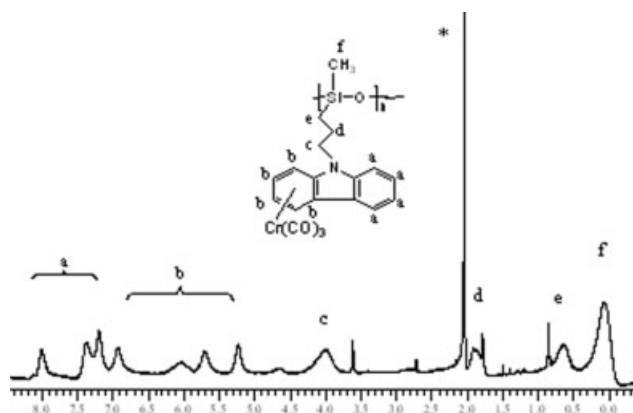

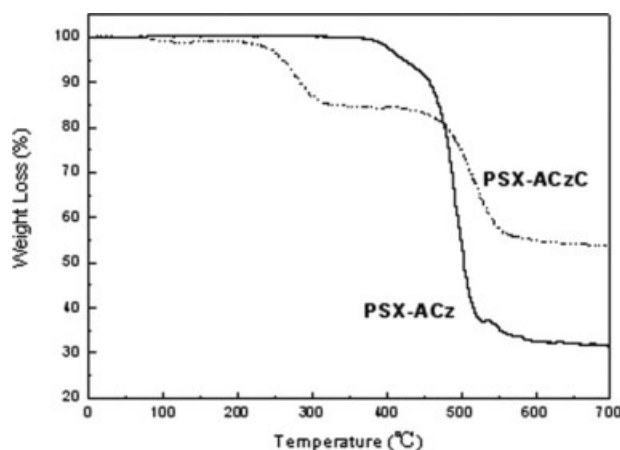**Figure 1** ¹H NMR spectrum of **PSX-ACzC** in CD₃COCD₃ (*, solvents) at room temperature.

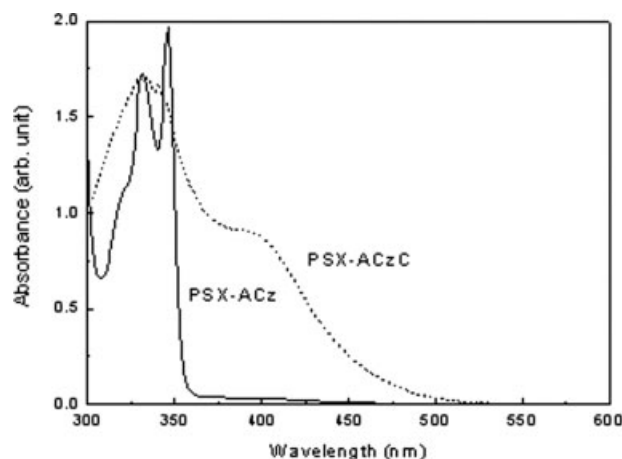**Figure 2** Thermal gravimetrical analysis of **PSX-ACz** and **PSX-ACzC**.

Figure 3 Electronic absorption spectra of **PSX-ACz** and **PSX-ACzC** films.

TABLE II
The Third-Order Nonlinear Optical Coefficients
of the Polymer Films

Polymer	$\chi^{(3)}$ of the films (10^{-13} esu)	n_2 (10^{-11} esu)	Thickness (nm)	T_d (°C)
PSX-ACz	0.49	0.14	343	510
PSX-ACzC	6.92	1.71	357	281

Linear and nonlinear optical properties

The electronic spectrum of **PSX-ACz** and **PSX-ACzC** film was shown in Figure 3. As shown clearly in Figure 3, **PSX-ACzC** had two characteristic absorption bands over a wide wavelength region[3,4,19–21] while its organic counterpart **PSX-ACz** behaved completely different. In both cases, the longest wavelength absorption band with a small extinction coefficient can be attributed to the metal-to-ligand charge-transfer (MLCT) arising from a charge transition from the chromium center to the π- and σ- bound ligands. Similarly, the shorter wavelength absorption band with a larger extinction coefficient can be assigned to the intra-ligand (IL) transition, mostly the π-π* transition. The detailed time-of-flight measurements have shown that **PSX-ACz** exhibited a charge carrier mobility that is about one order of magnitude higher than that of PVK.[22,23] Due to the amphoteric nature of electrons in $Cr(CO)_3$ moiety, the introduction of chromium tricarbonyl into polymers may increase the charge transfer in the polymers. Therefore, we expect that **PSX-ACzC** should have higher charge carrier mobility than **PSX-ACz**, and it is promising that polymer **PSX-ACzC** could to be used as a new electrons hole-transporting material.

The DFWM results were shown in Figure 4, in which the solid line represented the theoretical curve fitted by a Gaussian function. The third-order susceptibility, $\chi^{(3)}$ and the nonlinear refractive index, n_2, were also obtained, as listed in Table II. These results indicated that there was a significant contribution from chromium complexation to the magnitude of the third-order nonlinear response. In addition, the measured $\chi^{(3)}$ of **PSX-ACzC** was about one order of magnitude higher than that of **PSX-ACz**, showing a high dependence on the chromium tricarbonyl coordination. The significant increase in the magnitude of nonlinear response was mainly due to the introduction of transition metal atom Cr whose open d-shell participated in the low energy charge transfer and therefore made an important contribution to optical nonlinearity.[24]

loss of **PSX-ACzC** was probably caused by the liberation of carbon monoxide from the chromium center. The second stage weigh loss can be explained by the disruption of the main chain of **PSX-ACzC**. The glass transition temperature (T_g) of **PSX-ACz** and **PSX-ACzC** was determined by differential scanning calorimetry (DSC-200 PC, write manufacturer here) at the 10°C/min heating rate. In this manner, the glass transition temperature of **PSX-ACz** and **PSX-ACzC** was found to be 108°C and 57°C, respectively. It contrasts sharply with poly(N-vinylcarbazole chromium tricarbonyl), which either has no T_g or whose T_g is even higher than its decomposition temperature 290°C.[16] The reason that T_g of **PSX-ACzC** was much lower than that of poly(N-vinylcarbazole chromium tricarbonyl) is probably because of its flexible backbone, which optimizes its thermal stability. The appropriate T_g is an important performance issue for NLO devices.
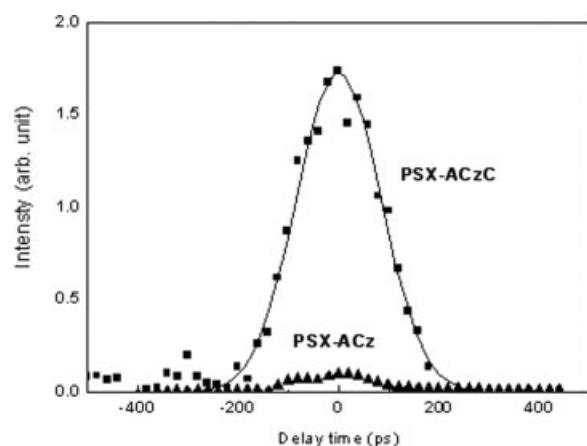

Figure 4 Temporal DFWM signals of **PSX-ACz** and **PSX-ACzC** films.

CONCLUSIONS

In summary, a novel η^6-complexe of N-allylcarbazole containing chromium tricarbonyl **ACzC** was synthesized. This complex was hydrosilylated with poly-

methylhydrosiloxane to afford a novel functionalized **PSX-ACzC**. The linear spectroscopic properties and the third-order optical nonlinearities of the polymer films as well as the thermal properties of the polymer were studied. The DFWM results suggested that chromium complexation can be one of the most effective ways to improve the nonlinear response. The transparent nature of polymethylhydrosiloxane fits well for organometallic chromophores, and hydrosilylated polymer is a suitable material for the of NLO devices. The incorporation of metallic center into a carbazole polysilane system seems to be a possible route for designing and synthesizing new type of carbazole-subsitituted polysilanes with improved material properties that are unobtainable in simple π-organic or organometallic systems.

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