9680 J. Am. Chem. Soc. 1998, 120, 9680−9681

Communications to the Editor

Synthesis of Bifunctional Photorefractive Polymers with Net Gain: Design Strategy Amenable to Combinatorial Optimization

Matthew S. Bratcher, Michael S. DeClue,
Anders Grunnet-Jepsen,[†] Daniel Wright, Barry R. Smith,
W. E. Moerner,* and Jay S. Siegel*

Department of Chemistry
University of California-San Diego
La Jolla, California 92093-0358

Received April 30, 1998

Present designs for photorefractive polymer materials require three principal components, a charge generator (CG); a charge transport agent (CTA) or photoconductor; and a nonlinear optical (NLO) chromophore (Figure 1).[1,2] Photoconducting polymers, doped with NLO and CG materials, have shown remarkable photorefractive effects but often lack appropriate materials properties (such as stability against crystallization) and are not amenable to simple combinatorial methods for optimization. Designer polymers with multiple components built into one covalent network demonstrate superior materials properties,[3−7] but typically require extensive monomer synthesis for each structural change.[8] An alternative design strategy is to begin with a polymer and graft on the components (Figure 2).[9−12] Herein, this strategy creates bifunctional polymers and leads to photorefractive materials, with net gain, derived from simple siloxane polymers and platinum catalyzed hydrosilation chemistry.[13]

The synthesis strategy pivots on the platinum-catalyzed hydrosilation of olefins with poly(hydromethyl)siloxane. This method has been previously used to prepare homopolymers with photoconducting properties (**1**).[14,15] Extension of the method to permit the incorporation of multiple olefins in the same reaction pot immediately opens up the possibility to synthesize a library of polymeric materials and to optimize their properties by combinatorial methods.[16−19] Initially, even parallel synthesis can lead rapidly to a prototype. In addition to the nature of the various components, the relative proportions can also be controlled. Thus, polymers of the general form xCG/yCTA/zNLO are attainable.[20]

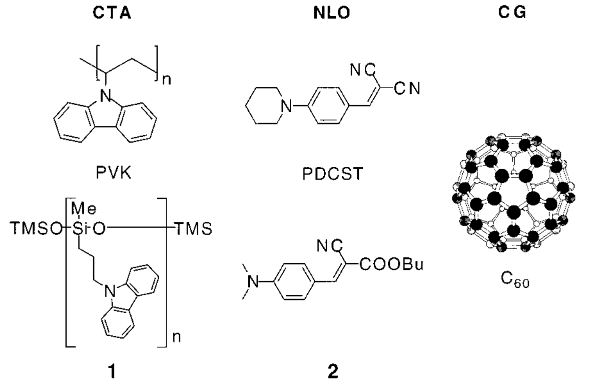


Figure 1. Examples of CTA, NLO, and CG materials commonly used for photorefractive polymer composites.

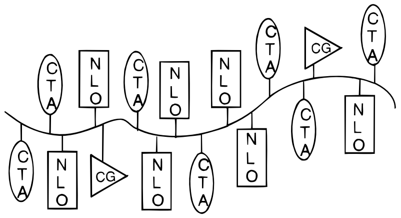


Figure 2. Generalized fully functional photorefractive polymer: CG, Charge Generator; CTA, Charge Transport Agent; NLO, Non-Linear Optical chromophore.

Starting out to mimic the known active polymer composite of PDCST/PVK/C_{60},[21,22] we prepared allylcarbazole, purchased allylcyanoacetate,[23] and ran the mixed hydrosilation reaction in the presence of platinum catalyst with toluene as solvent (Scheme 1). Purification was achieved by an initial toluene/methanol precipitation, followed by a repetitive reprecipitation procedure using tetrahydrofuran as solvent and hexanes as precipitant. The mixed, grafted polymer was then subjected to Knovenagel conditions with para-*N*,*N*-dimethylaminobenzaldehyde in tetrahydrofuran, **3**, **4**, and **5**. In parallel, the same reaction sequence was run using 5-pentenylcarbazole to modulate the carbazole mobility and give **6** (CTA/NLO = 1.8). This approach provided materials that vary in CTA-chain length and CTA/NLO ratios.

Siloxane polymers of this type typically have low T_g and relatively high solubility in solvents such as tetrahydrofuran and toluene, which facilitates spectroscopic characterization by NMR,

---

[†] Present address: Templex Technology, Eugene, OR 97401.

(1) Moerner, W. E.; Silence, S. M. *Chem. Rev.* **1994**, *94*, 127−155.

(2) Moerner, W. E.; Grunnett-Jepsen, A.; Thompson, C. L. *Annu. Rev. Mater. Sci.* **1997**, *27*, 585−623.

(3) Bolink, H. J.; Arts, C.; Krasnikov, V. V.; Malliaras, G. G.; Hadziioannou, G. *Chem. Mater.* **1997**, *9*, 1407−1413.

(4) Zhang, Y.; Wada, T.; Wang, L.; Sasabe, H. *Tetrahedron Lett.* **1997**, *38*, 1785−1788.

(5) Zhang, Y.; Wang, L.; Wada, T.; Sasabe, H. *Macromol. Chem. Phys.* **1996**, *197*, 667−676.

(6) (a) Yu, L.; Chen, Y. M.; Chan, W. K. *J. Phys. Chem.* **1995**, *99*, 2797−2802. (b) Yu, L.; Chan, W.; Bao, Z.; Cao, S. X. F. *J. Chem. Soc., Chem. Commun.* **1992**, 1735−1737.

(7) Zhao, C.; Park, C.-K.; Prasad, P. N.; Zhang, Y.; Ghosal, S.; Burzynski, R. *Chem. Mater.* **1995**, *7*, 1237−1242.

(8) Yu, L.; Chan, W. K.; Peng, Z.; Gharavi, A. *Acc. Chem. Res.* **1996**, *29*, 13-21.

(9) Strohriegl, P. *Makromol. Chem.* **1993**, *194*, 363−387.

(10) Staufer, G.; Lattermann, G. *Makromol. Chem.* **1991**, *192*, 2421−2431.

(11) Chang-Chien, G.-P.; Kuo, J.-F. *J. Appl. Polym. Sci.* **1995**, *57*, 1183−1204.

(12) Chang-Chien, G.-P.; Kuo, J.-F. *Liq. Cryst.* **1996**, *20*, 705−714.

(13) CG's are typically added in less that 1% as a dopant. In principle, "fully-functional" material could also be produced by covalent attachment of C60 to the siloxane, work in progress.

(14) Strohriegl, P. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 771−5.

(15) Lux, P.; Strohriegl, P.; Höcker, H. *Makromol. Chem.* **1987**, *188*, 811−820.

(16) Danielson, E.; Golden, J. H.; McFarland, E. W.; Reaves, C. M.; Weinberg, W. H.; Wu, X. D. *Nature* **1997**, *389*, 944−48.

(17) Xiang, X. D.; Sun, X.; Briceno, G.; Lou, Y.; Wang, K.-A.; Cheng, H.; Wallace-Freedman, W. G.; Chen, S.-W.; Shultz, P. G. *Science* **1995**, *268*, 1738−40.

(18) Combinatorial polymer arrays with controlled T_g and wetting angles have been prepared by AB polymerization, see: Brocchini, S.; James, K.; Tangpasuthadol, V.; Kohn, J. *J. Am. Chem. Soc.* **1997**, *119*, 4553−4554.

(19) (a) A mixed-feed grafting approach was used to develop a polymer-supported catalyst, see: Menger, F. M.; Eliseev, A. V.; Migulin, V. A. *J. Org. Chem.* **1995**, *60*, 6666−6667. (b) Menger, F. M.; West, C. A.; Ding, J. *J. Chem. Soc., Chem. Commun.* **1997**, 633−634.

(20) A focused library of 20 bifunctional materials has been prepared: manuscript in preparation.

(21) Silence, S. M.; Donckers, M. C. J. M.; Walsh, C. A.; Burland, D. M.; Twieg, R. J.; Moerner, W. E. *Appl. Opt.* **1994**, *33*, 2218−2222.

(22) Grunnet-Jepsen, A.; Thompson, C. L.; Twieg, R. J.; Moerner, W. E. *Appl. Phys. Lett.* **1997**, *70*, 1515.

(23) Commercial products: allylcycanoacetate (Aldrich); Poly(hydromethyl)siloxane (Aldrich).

S0002-7863(98)01473-5 CCC: $15.00

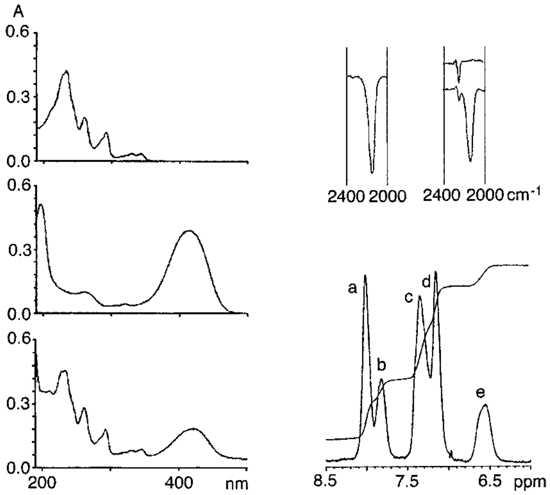
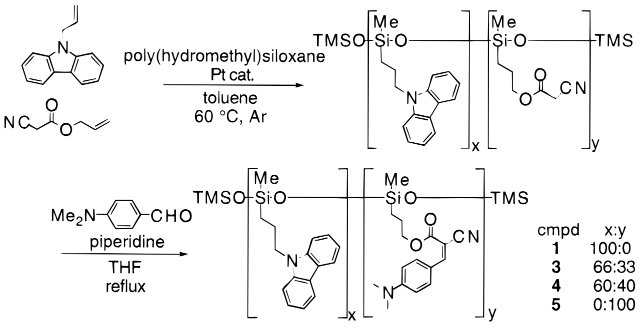


Figure 3. Spectral characterization: left top, UV of **1**; middle, UV of **5**; bottom, UV of **4**; right-top-left, IR of Si−H region starting siloxane; right-top-right, IR of Si−H region at the start and end of the reaction (the small absorbance to the left of Si−H is RCN from the NLO); right bottom, ^{1}H NMR of **4** with integral for determining molar ratios of NLO:CTA (see Table 1); NLO, (peaks a, b, and e); CTA, (peaks a, c, and d).

Scheme 1



IR, and UV methods. Reaction progress is monitored by the residual Si−H stretch that comes in a convenient window of the IR spectrum (2160 cm^{-1}). Incorporation ratios of the olefins can be determined by integration of the NMR signals assigned to specific components and by the UV absorptions accounting for the relative molar absorptivity. NMR and UV methods also show that the discrete spectroscopic signatures of the molecular components are not lost or significantly perturbed in the polymer (Figure 3). The commercial siloxanes used in this study have a broad molecular weight distribution,[23] and GPC analysis confirms that this breadth of distribution is carried through to the product functionalized polymer.

The photorefractive properties of these materials were investigated through a classical two-beam coupling experiment.[24] In this experiment, a grating is formed by crossing two coherent laser beams in a material across which an electric field is applied. Through the photorefractive effect, power is transferred from one beam to the other, and when the transfer of power exceeds the absorption by the sample, a condition of net gain is achieved. Photorefraction is seen for each of the bifunctional polymers described here, and sample **4** showed a net gain (Table 1).[25] As a comparison, a composite of **1**, **2**, and C_{60} (1.5:1:0.02) was prepared (**7**). The processing of the sample required much higher temperatures, and problems with crystallization plagued the sample preparation. Finally, a reasonable sample of **7** was prepared, but it showed a gain significantly lower than the comparable bifunctional **4**, thus, supporting the practical aspects of the grafting methodology.

Table 1. Physical and Photorefractive Characterization of **3**, **4** and **7**

sample	3	4	7
T_g (°C)^a	25	43	30
ratio (CTA/NLO)^b	2	1.5	1.5
$T_{prep}{}^c$	70	50	123
$R \times 10^{-18}$ (m2/V2)^d	0.15	0.15	0.16
σ_{dark} (pS/cm)^e	0.005	0.005	0.003
σ_{photo} (pS/cm)^e	0.005	0.016	0.020
gain coeff Γ (cm^{-1})^f	4	22	12
τ (s)^g	10	2.8	1.8
α (cm$^{-1)h}$	16	5.4	5.4

[a] Glass transition temperature measured by DSC. [b] Molar ratio of CTA/NLO as determined by NMR and UV. [c] Processing temperature to make good samples. [d] Quadratic NLO response at 1 Hz[26] [e] Conductance dark and photo at 40 mW/cm^2. [f] Gain coefficient.[24] [g] Response time at 0.25 W/cm^2. [h] Absorbance at 676 nm. [i] Trap density.[24]

These results prove not only that this method is useful for the rapid and variable synthesis of bicomponent polymeric materials but also that these materials can be highly active in the photonic and electronic applications for which they were designed. The proof of principle having been established, it remains for a general library to be elaborated.

This method will be applied to the rational design of structure−function assays such as those related to the recently discovered relationship between HOMO energies and trapping densities.[27] It is our hope that the generality of this synthetic method applies far beyond the development and optimization of photorefractive materials; specifically, we anticipate libraries of siloxane-based polymer grafts as catalysts, sensors, and materials.

Acknowledgment. This work is supported by the U.S. National Science Foundation (CHE-9628565) and US-AFOSR (F4962096-1-0135 and F49620-97-1-0286).

JA981473X

---

(24) Sample preparation and experimental methods are described in Grunnet-Jepsen, A.; Thompson, C. L.; Moerner, W. E. *J. Opt. Soc. Am. B* **1998**, *15*, 905. Applied field 40 V/μm for Γ and τ, 20 V/μm for σ.

(25) Preliminary data on **6** with the carbazole connected to the backbone by five methylenes shows promising results; cf., $T_g = 26$; molar ratio of CTA/NLO = 1.8; $\sigma_{dark} = 0.012$; $\sigma_{photo} = 0.002$; $\Gamma = 7$; $\alpha = 10.4$; $\tau = 41$. Applied field 40 V/μm (see Table 1 for explanation of symbols).

(26) Sandalphon; Kippelen, B.; Meerholz, K.; Peyghambarian, N. *Appl. Opt.* **1996**, *35*, 2346−2354.

(27) Grunnet-Jepsen, A.; Wright, D.; Smith, B.; Bratcher, M. S.; DeClue, M. S.; Siegel, J. S.; Moerner, W. E. *Chem. Phys. Lett.* **1998**, *291*, 553−561.