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Frontal Polymerization with Thiol−Ene Systems

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Introduction. Frontal polymerization entails the conversion of a monomer into a polymer via a localized exothermic reaction zone that propagates through the coupling of thermal diffusion and Arrhenius reaction kinetics. Frontal polymerization was discovered in Russia by Chechilo and Enikolopyan in 1972 using methyl methacrylate under high pressure.[1] The extensive work from Russia was reviewed by Davtyan et al.[2]

Pojman and co-workers performed an extensive study of the macrokinetics and dynamics of frontal polymerization.[3−7] They recently studied frontal copolymerization.[8] Frontal polymerization has been used to prepare different materials, including thermochromic composites,[9] IPNs,[6] polymer-dispersed liquid crystal materials,[10] functionally gradient materials,[11−13] and large composites.[14]

An overwhelming majority of work has been on free-radical systems, but other chemistries can be used. Begishev et al. studied frontal anionic polymerization of ϵ-caprolactam,[15,16] and epoxy chemistry has been used as well.[17−20] Mariani et al. demonstrated frontal ring-opening metathesis polymerization,[21] and Fiori et al. produced polyacrylate/poly(dicyclopentadiene) networks frontally.[22] Polyurethanes have recently been prepared frontally.[23,24] Frontal atom transfer radical polymerization has recently been achieved.[25]

Thiols can form polymers with ene compounds via a free-radical step-growth mechanism.[26−33] These systems are especially interesting because of reduced sensitivity to oxygen that plagues traditional acrylate polymerizations.[26,31] In the absence of oxygen, the two-step polymerization mechanism consists of a radical addition of the thiyl radical to the carbon−carbon double bond of a reactive ene. The carbon-centered radical readily abstracts a hydrogen in a chain transfer step. In cases where the ene does undergo a homopolymerization process, the only reaction is cross-linking copolymerization when the thiol and ene have an average functionality greater than two.

Herein, we examine for the first time the frontal polymerization of two types of thiol−ene systems: a trithiol with a triallyl ether that proceeds to give a cross-linked network by a free-radical step growth copolymerization mechanism and a trithiol with a diacrylate, which can also undergo free-radical chain homopolymerization. In both cases we used (1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane) as the free-radical peroxide initiator.

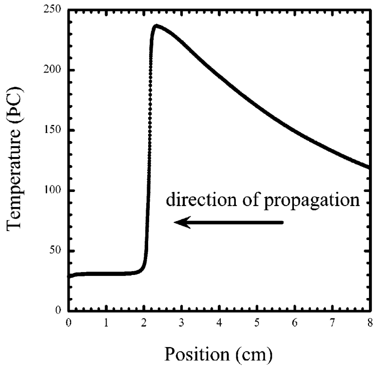

Figure 1. Temperature profile for a 1:1 PTE:TT1 front with 2% Luperox 231 initiator.

Experimental Section. We performed all experiments in glass tubes, 16 × 125 mm (VWR #72690-022), on which a plastic cap (VWR #60826-290) could be securely screwed. Polymerization was initiated by heating the wall of the tube with a soldering iron. Fronts were always performed in the descending mode to avoid buoyancy-driven convection.[34] The reproducibility of velocity measurements was ±10%.

The solutions were degassed for 10 min with a vacuum pump in order to remove most of the dissolved air in order to avoid bubble formation that would interfere with accurate front velocity determinations.[5] However, no attempt was made to completely remove oxygen.

Temperature profiles were measured by using copper−constantan thermocouples with a wire diameter of 0.075 mm. The temporal profile was converted to a spatial one using the front velocity.[35]

Pentaerythrytoltriallyl ether (PTE) (75%), trimethylolpropane tris(3-mercaptopropionate) (95%) (TT1), and 1,6-hexanedioldiacrylate (80%, technical grade) (HDDA) were obtained from Aldrich and used as received. The mole fractions were determined from the functionality of each component and its reported purity.

Luperox 231 ((1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane)) was obtained from Atofina.

Results and Discussion. The position vs time data for all systems were linear. The linear dependence indicates that a constant-velocity, self-sustaining front was achieved. Figure 1 shows a front temperature profile. It is interesting to note that despite the high front temperature, the pure thiol−ene system has a relatively low front velocity, on the order of 1 cm min^{-1}. HDDA fronts with 2% initiator had a velocity of 6.4 cm min^{-1}.

It is well-known that thiols with allyl ethers react by a free-radical step-growth mechanism.[26−30,32,33] Because a step-growth mechanism is a reaction with a defined stoichiometry, we expected that there should be an optimal ratio of the thiol and ene. We confirmed this by determining the front velocity as a function of the thiol−ene ratio, which was a maximum at the stoichiometric mixture (1:1) (Figure 2). Nonstoichiometric ratios can sustain a front over a limited range (0.4−0.68), but outside this range the exotherm generated is not suf-

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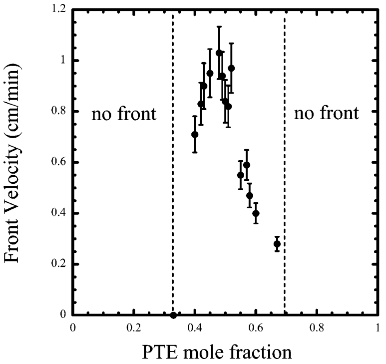

Figure 2. Front velocity of the PTE−TT1 thiol−ene fronts for 2% (v/v) Luperox 231 as a function of the PTE mole fraction.

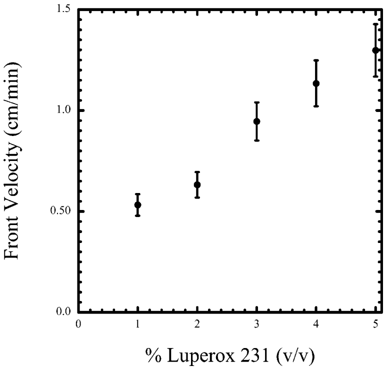

Figure 3. Front velocity for a 1:1 PTE:TT1 system as a function of the initiator concentration.

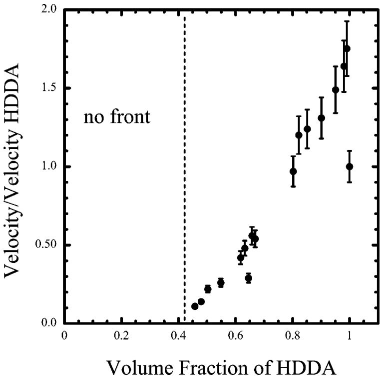

Figure 4. Front velocity dependence on the fraction of HDDA with TT1 with 2% (v/v) Luperox 231. The front velocity of the pure HDDA front was 6.4 cm min^{-1}.

ficient to sustain a front with the amount of heat loss from the tube.

Figure 3 shows the velocity dependence as a function of the peroxide concentration for the stoichiometric TT1:PTE mixture. As has been seen in free-radical chain growth frontal polymerization, the velocity increases monotonically with the initiator concentration.[5,36]

Frontal polymerization with acrylates has been shown to exhibit nonplanar modes of polymerization in which the front propagates as a helix.[5,37−39] We observed spin modes for mole fractions of PTE between 0.58 and 0.60 and 0.33 and 0.43. Why spin modes should only be observed for nonstoichiometric mixtures is not clear and is under investigation.

We also studied a thiol−diacrylate (HDDA) system in which the ene could undergo both copolymerization with the thiol and chain polymerization. Figure 4 shows the velocity dependence on the fraction of HDDA with TT1. We first notice that the front velocity exhibits a maximum at a TT1 concentration near 1%. The increase in the front velocity with small amounts of thiol is related to oxygen inhibition. A particularly attractive feature of thiol−ene chemistry is the insensitivity to oxygen inhibition that is exhibited by acrylates.[31] In the present case, small amounts of thiols are effective because the alkyl peroxy radicals that are formed abstract a hydrogen from the thiol to produce a reactive thiyl radical, which reinitiates the radical polymerization of the acrylate. Thus, the thiol increased the front velocity by reducing the inhibition of oxygen. As more and more thiol was added, the lower reactivity of the thiol dominated, and the front velocity decreased. For samples with greater than 60% TT1, the systems could not support frontal polymerization due to the unreacted thiol groups.

This observation can be quite important for potential applications. There is a practical limit to how much peroxide can be added to increase the front velocity, but adding only small amount of a thiol can give an increase that can make a frontal system propagate faster.

Conclusions. We demonstrated for the first time frontal polymerization in multifunctional thiol−ene systems. For an ene that could not undergo free-radical-chain propagation, the front velocity and front temperature were a maximum at the stoichiometric ratio of the thiol and ene. For a system like HDDA, which can homopolymerize as well as copolymerize with the thiol, the addition of even a small amount of thiol increased the front velocity by as much as 80% by reducing oxygen inhibition.

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References and Notes

(1) Chechilo, N. M.; Khvilivitskii, R. J.; Enikolopyan, N. S. *Dokl. Akad. Nauk S.S.S.R.* **1972**, *204*, 1180−1181.
(2) Davtyan, S. P.; Zhirkov, P. V.; Vol'fson, S. A. *Russ. Chem. Rev.* **1984**, *53*, 150−163.
(3) Pojman, J. A.; Willis, J.; Fortenberry, D.; Ilyashenko, V.; Khan, A. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 643−652.
(4) Pojman, J. A.; Curtis, G.; Ilyashenko, V. M. *J. Am. Chem. Soc.* **1996**, *118*, 3783−3784.
(5) Pojman, J. A.; Ilyashenko, V. M.; Khan, A. M. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2825−2837.
(6) Pojman, J. A.; Elcan, W.; Khan, A. M.; Mathias, L. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 227−230.
(7) Fortenberry, D. I.; Pojman, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1129−1135.
(8) Perry, M. F.; Volpert, V. A.; Lewis, L. L.; Nichols, H. A.; Pojman, J. A. *Macromol. Theory Simul.* **2003**, *12*, 276−286.
(9) Nagy, I. P.; Sike, L.; Pojman, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 3611−3612.
(10) Gill, N.; Pojman, J. A.; Willis, J.; Whitehead, J. B. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 204−212.
(11) Chekanov, Y. A.; Pojman, J. A. *J. Appl. Polym. Sci.* **2000**, *78*, 2398−2404.
(12) Pojman, J. A.; McCardle, T. W. The University of Southern Mississippi, U.S. Patent, 2000.
(13) Pojman, J. A.; McCardle, T. W. The University of Southern Mississippi, U.S. Patent, 2001.
(14) Kim, C.; Teng, H.; Tucker, C. L.; White, S. R. *J. Comput. Mater.* **1995**, *29*, 1222−1253.
(15) Begishev, V. P.; Volpert, V. A.; Davtyan, S. P.; Malkin, A. Y. *Dokl. Akad. Nauk S.S.S.R.* **1973**, *208*, 892.
(16) Begishev, V. P.; Volpert, V. A.; Davtyan, S. P.; Malkin, A. Y. *Dokl. Phys. Chem.* **1985**, *279*, 1075−1077.

(17) Davtyan, S. P.; Arutyunyan, K. A.; Shkadinskii, K. G.; Rozenberg, B. A.; Yenikolopyan, N. S. *Polym. Sci. U.S.S.R.* **1978**, *19*, 3149−3154.

(18) Korotkov, V. N.; Chekanov, Y. A.; Rozenberg, B. A. *Comput. Sci. Technol.* **1993**, *47*, 383−388.

(19) White, S. R.; Kim, C. *J. Reinf. Plast. Comput.* **1993**, *12*, 520−535.

(20) Chekanov, Y.; Arrington, D.; Brust, G.; Pojman, J. A. *J. Appl. Polym. Sci.* **1997**, *66*, 1209−1216.

(21) Mariani, A.; Fiori, S.; Chekanov, Y.; Pojman, J. A. *Macromolecules* **2001**, *34*, 6539−6541.

(22) Fiori, S.; Mariani, A.; Ricco, L.; Russo, S. *e-Polym.* **2002**, *29*, 1−10.

(23) Fiori, S.; Mariani, A.; Ricco, L.; Russo, S. *Macromolecules* **2003**, *36*, 2674−2679.

(24) Mariani, A.; Bidali, S.; Fiori, S.; Malucelli, G.; Sanna, E. *e-Polym.* **2003**, *44*, 1−9.

(25) Bidali, S.; Fiori, S.; Malucelli, G.; Mariani, A. *e-Polym.* **2003**, *060*, 1−12.

(26) Jacobine, A. F. In *Radiation Curing in Polymer Science and Technology*; Fouassier, J. P., Ed.; Elsevier: New York, 1993; pp 219−268.

(27) Cramer, N. B.; Scott, J. P.; O'Brein, A. K.; Bowman, C. N. *Macromolecules* **2003**, *35*, 4631−4636.

(28) Cramer, N. B.; Davies, T.; O'Brein, A. K.; Bowman, C. N. *Macromolecules* **2003**, *35*, 5361−5365.

(29) Morgan, C. R.; Magnotta, F.; Ketley, A. D. *J. Polym. Sci., Part A: Polym. Chem.* **1977**, *15*, 627.

(30) Morgan, C. R.; Ketley, A. D. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 75.

(31) Gush, D. P.; Ketley, A. D. *Mod. Paint Coat.* **1978**, *68*, 61.

(32) Hoyle, C. E.; Cole, M.; Bachemin, M.; Yoder, B.; Mguyen, C.; Jonsson, S. *Polym. Prepr.* **2001**, *42*, 697−698.

(33) Hoyle, C. E.; Cole, M.; Bachemin, M.; Kuang, W.; Kalyanaraman, V.; Jonsson, S. In *Photoinitiated Polymerization;* ACS Symposium Series No. 793; Belfield, K. D., Crivello, J. V., Eds.; American Chemical Society: Washington, DC, 2003; pp 52−64.

(34) Bowden, G.; Garbey, M.; Ilyashenko, V. M.; Pojman, J. A.; Solovyov, S.; Taik, A.; Volpert, V. *J. Phys. Chem. B* **1997**, *101*, 678−686.

(35) Pojman, J. A.; Craven, R.; Khan, A.; West, W. *J. Phys. Chem.* **1992**, *96*, 7466−7472.

(36) Goldfeder, P. M.; Volpert, V. A.; Ilyashenko, V. M.; Khan, A. M.; Pojman, J. A.; Solovyov, S. E. *J. Phys. Chem. B* **1997**, *101*, 3474−3482.

(37) Pojman, J. A.; Masere, J.; Petretto, E.; Rustici, M.; Huh, D.-S.; Kim, M. S.; Volpert, V. *Chaos* **2002**, *12*, 56−65.

(38) Masere, J.; Stewart, F.; Meehan, T.; Pojman, J. A. *Chaos* **1999**, *9*, 315−322.

(39) Pojman, J. A.; Volpert, V. A.; Volpert, V. A. In *Self-Propagating High-Temperature Synthesis of Materials*; Borisov, A. A., De Luca, L. T., Merzhanov, A. G., Eds.; Taylor and Francis: New York, 2002; pp 99−118.

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