further confirmed by subjecting **4** to thermal deblocking at 200 °C, which results in isocyanate (2260 cm^{-1}) formation. The identity of compounds **3** and **4** was established by a two-step parallel synthesis(II) of **5** and **6** and similarities of IR spectra. However, compound **3** also shows peaks at 1680 cm^{-1}, corresponding to urea linkages. Thus the product profile results are similar to that of nitrobenzene leading to carbamate, aniline, and diphenylurea.[5] Collman[11] proposed the method to differentiate homogeneous and heterogeneous hydrogenation catalysts based on their reactivity toward polymeric substrates. Only the soluble molecular catalysts have been found to interact with functional groups attached to insoluble polymer networks. The present work is an extension of carbonylation reaction to polymeric substrates and may be indicative of a truly homogeneous nature of the catalysts.

Our methodology offers a novel phosgene-free, isocyanate-free route to polyurethane coatings and provides a new formulation latitude. The reaction conditions have not been optimized. The key variables in the design of polymeric cross-linker are (1) backbone composition, (2) molecular weight, and (3) functionality. Clearly, the metal carbonyl/cocatalyst system has a very significant influence on the reaction pathway.[12]

Acknowledgment. We thank Drs. B. N. Roy and K. Srinivasan for helpful discussions and Mr. N. V. Joshi for experimental assistance. Financial support was provided by ICI India Ltd.

References and Notes

(1) Potter, T. A.; Williams, J. L. *J. Coat. Technol.* **1987**, *59* (749), 63.
(2) Klein, D., et al. *J. Paint Technol.* **1971**, *43* (562), 68–75.
(3) Wicks, Z. *Prog. Org. Coat.* **1981**, *9*, 2–28.
(4) Cenini, S.; Crotti, C.; Pizzotti, M.; Porta, F. *J. Org. Chem.* **1988**, *53*, 1243.
(5) Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F. *J. Chem. Soc., Chem. Commun.* **1984**, 1286.
(6) Bhaduri, S.; Khwaja, H.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1988**, 194.
(7) Bhaduri, S.; Khwaja, H.; Sharma, K.; Jones, P. G. *J. Chem. Soc., Chem. Commun.*, in press.
(8) *Reactions of Polymers*; Moore, J. A., Ed. Reidel: Dordrecht, Holland, 1973; pp 153.
(9) *Modification of Polymers*; Carraher, C. E., Tsuda, M., Eds.; American Chemical Society: Washington, DC, 1980; p 1.
(10) Kucharski, M. *Polimery* **1966**, *11*, 253 (*Chem. Abstr.* **1967**, *66*, 2855).
(11) Collman, J. P.; Kosydar, K. M.; Bresan, M.; Lamanna, W.; Garrett, T. *J. Am. Chem. Soc.* **1984**, *106*, 2569.
(12) Williams, G. D.; Whittle, R. R.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 3936.

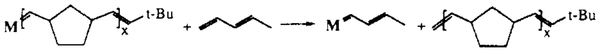
Registry No. $NEt_4^+Cl^-$, 56-34-8; methanol, 67-56-1; $Ru_3(CO)_{12}$, 15243-33-1.

Communications to the Editor

Chain-Transfer Agents for Living Ring-Opening Metathesis Polymerization Reactions of Norbornene

Catalysts of the type $M(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (M = Mo[1] or W[2]) have now been used to polymerize norbornene,[3] 5,6-disubstituted norbornadienes (stereoselectively),[4] and 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene[5] by living ring-opening metathesis polymerization (ROMP).[6] Living ROMP requires that a propagating alkylidene complex react only with monomer, not with the substituted double bonds in the polymer chain. Up to now, the living polymer has been quenched with an aldehyde in order to remove the metal and cap the polymer in a Wittig-like reaction. A chain-transfer (CT) agent for these relatively unreactive complexes would be much more desirable. An initial search for a suitable CT agent focused on substituted cyclopentenes.[7] These chain-transfer agents were relatively unsuccessful because the cyclopentene bond was not reactive enough relative to a double bond in a side chain. We now find that 1,3-dienes and styrene work well as chain-transfer agents with the $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ catalyst and, if the monomer in question is reactive enough (e.g., norbornene), that it is possible to pulse the system with monomer in the presence of the CT agent to give polymers with relatively low polydispersities.

Vinylalkylidene complexes are observable intermediates in reactions in which 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene[5] or acetylene[6b] is polymerized and were found to be relatively stable. A number of simpler vinylalkylidene complexes have subsequently been prepared and isolated by reaction of *cis*- or *trans*-1,3-pentadiene with $M(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ or $M(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2$ (M = Mo or W) in the presence of a suitable Lewis base.[8] When less reactive neopentylidene complexes $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ or $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ were treated with 1,3-pentadiene, the initiator was slowly consumed but no new alkylidene complexes were observed. However, living polymers derived from norbornene were found to react rapidly with 1,3-pentadiene to generate vinylalkylidene complexes $M(CHCH{=}CHMe)(NAr)(O\text{-}t\text{-}Bu)_2$ and capped polymers (eq 1). Although the tungsten vinylalkylidene complex decomposed in C_6D_6 over the course of several hours, the molybdenum complex[9] proved to be stable at a concentration of ~0.01 M for 24 h.



(1)

M = $Mo(NAr)(O\text{-}t\text{-}Bu)_2$

The observation that living polyenes derived from acetylene are excellent initiators for ROMP[6b] suggested that the in situ generated vinylalkylidene complexes described

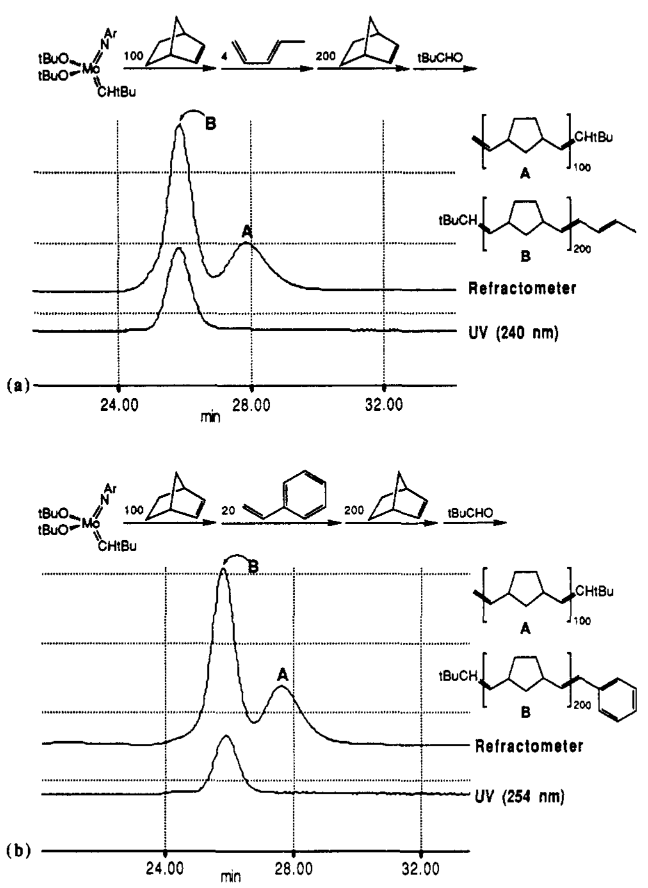
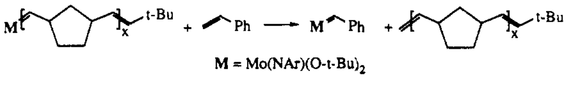


Figure 1. (a) GPC trace of product from chain-transfer experiment using *trans*-1,3-pentadiene as CT agent. PDI = 1.05 for polymer derived from vinylalkylidene initiator (UV trace). (b) GPC trace of product from chain-transfer experiment using styrene as CT agent. PDI = 1.07 for polymer derived from benzylidene initiator (UV trace).

above should also be good initiators. This proved to be the case. *trans*-1,3-Pentadiene was found to be an effective chain-transfer agent in norbornene polymerization. When Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (typically 10–20 mg in 10 mL of toluene) was treated with 100 equiv of norbornene followed (after 10 min) by 4 equiv of *trans*-1,3-pentadiene, the initial yellow solution became red within 15 min, a color attributable to the vinylalkylidene complex, Mo(CHCH=CHMe)(NAr)(O-*t*-Bu)$_2$. When this red solution was treated with an additional 200 equiv of norbornene, a yellow (living polymer) solution resulted which turned red (vinylalkylidene) again over 15–20 min. GPC analysis (Figure 1a) of the resulting sample showed that two polymeric products were present with molecular size (versus polystyrene) and UV spectra consistent with their being t-BuCH(CHC$_5$H$_8$CH)$_{100}$CH$_2$ (100-mer; PDI = M_w/M_n = 1.05) and MeCH=CHCH(CHC$_5$H$_8$CH)$_{200}$CH$_2$ (200-mer; PDI = 1.05). The narrowness of the two peaks and the absence of a 300-mer peak (shown to be nearly resolvable from the 200-mer) indicate that both chain transfer and subsequent initiation of the second polymer chain are well-behaved.

Styrene also is a well-behaved chain-transfer agent. Living polynorbornene was found to react with styrene to generate Mo(CHPh)(NAr)(O-*t*-Bu)$_2$ and methylene-capped polynorbornene (eq 2).[10] Mo(CHPh)(NAr)(O-*t*-Bu)$_2$ can be prepared by treating Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ with excess styrene (~5 equiv) and was found to be stable in benzene solution (~0.04 M) for days, but decomposed upon isolation as a solid. When Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ was treated with 100 equiv of norbornene (10-min reaction time), then 20 equiv of styrene (30-min reaction time), and finally 200 equiv of norbornene (40-min reaction time), two polymeric products were obtained with molecular size and UV properties consistent with t-BuCH(CHC$_5$H$_8$CH)$_{100}$CH$_2$ (PDI = 1.05) and PhCH(CHC$_5$H$_8$CH)$_{200}$CH$_2$ (PDI = 1.07; Figure 1b).



(2)

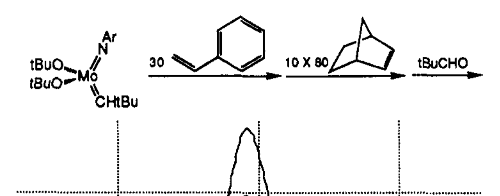


Figure 2. GPC trace of product from reaction where catalyst has been pulsed 10 times with 80 equiv of norbornene. PDI = ca. 1.07 for the main peak and 1.13 for the entire distribution (refractometer trace).

An experiment designed to determine if the CT agent can be present in excess and norbornene added in batches consisted of treating a mixture of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and styrene (30 equiv) at 40-min intervals with 10 portions of 80 equiv of norbornene. A polymer resulted that had approximately the weight average expected for an 80-mer and a polydispersity of 1.07 for the main peak (Figure 2; the main peak is ~95% of the total; PDI = 1.13 for the entire distribution). Qualitatively similar results were obtained in analogous experiments where *trans*-1,3-pentadiene was employed as the chain-transfer agent. However, in the cases examined thus far, lower polydispersities have been observed with 1,3-pentadiene as the CT agent.

Chain transfer employing 2,3-bis(trifluoromethyl)norbornadiene as the monomer in the presence of styrene gave a distribution of low molecular weight oligomers, a result that suggests that styrene reacts with the living alkylidene at a rate comparable to that of 2,3-bis(trifluoromethyl)norbornadiene (a relatively unreactive monomer compared to norbornene[4b]); i.e., the rates of chain transfer and chain growth are roughly comparable. The success of pulsed chain transfer understandably will depend upon the relative reactivities of the CT agent and the monomer in question. Since styrenes are readily available in wide variety,[11] it may be possible to vary the reactivity of the CT agent so that even monomers that are significantly less reactive than norbornene can be successfully polymerized in a pulsed experiment.

Finally, ordinary terminal olefins such as 1-pentene failed as chain-transfer agents, even in a two-step reaction. Two likely possible reasons are that they do not react rapidly enough with the living norbornene or that the resulting alkylidene complexes are not sufficiently stable.

Chain-transfer agents should allow well-characterized catalysts for polymer synthesis to be used more efficiently, especially in a continuous (pulsed) mode, assuming that the rate of reaction of the monomer is large relative to the rate of reaction of the chain-transfer agent. Pulsing experiments also should allow polymodal blends to be prepared in one pot.

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Acknowledgment. R.R.S. thanks the Office of Naval Research for support (Contract N00014-87-K-0099), W.E.C. thanks the National Institutes of Health for a postdoctoral fellowship, J.P.M. thanks SERC for a studentship and the Society of Chemical Industry (U.K.) for a Messel Scholarship, and we all thank NATO for a grant that has helped make this collaboration possible.

References and Notes

(1) (a) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373. (b) Schrock, R. R.; Murdzek, J. S.; Bazan, G.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(2) (a) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics*, in press.

(3) Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169.

(4) (a) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C. *Polym. Commun.* **1989**, *30*, 258. (b) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J., submitted for publication.

(5) Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989.

(6) (a) These catalysts have also been used to polymerize acetylene[6b] and benzvalene.[6c] (b) Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004. (c) Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 4413.

(7) Schrock, R. R.; Yap, K. B.; Yang, D. C.; Sitzmann, H.; Sita, L. R.; Bazan, G. *Macromolecules* **1989**, *22*, 3191.

(8) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; Davis, W. M.; O'Regan, M.; Schofield, M. H., submitted.

(9) ^1H NMR δ 12.00 (d, 1, $J = 9.5$ Hz, H_α), 7.92 (ddq, 1, $J = 14.9$, 9.5, 1.8 Hz, H_β), 4.77 (dq, 1, $J = 14.9$, 7.0 Hz, H_γ), 4.10 (sept, 2, $J = 6.9$ Hz, $C\mathit{H}Me_2$). Other resonances are obscured by resonances for polynorbornene.

(10) ^1H NMR (C_6D_6) δ 12.09 (s, 1, $C\mathit{H}Ph$), 4.02 (sept, 2, $C\mathit{H}Me_2$), 1.33 (s, 18, $C\mathit{Me}_3$), 1.23 (d, 12, $CH\mathit{Me}_2$), 7.0–7.2 (overlapping multiplets, aryl hydrogen atoms); ^{13}C NMR (C_6D_6) δ 247.8 (d, $J_{CH} = 125.1$ Hz, $\mathit{C}HPh$).

(11) Preliminary experiments indicate that *p*-methoxystyrene is an effective chain-transfer reagent. Treatment of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ with 100 equiv of norbornene (10-min reaction time), then 20 equiv of *p*-methoxystyrene (30 min), and finally 200 equiv of norbornene (10-min reaction time) gave a 100-mer and a 200-mer with a PDI (both peaks together) of 1.17. A pulsing experiment involving addition of 5 portions of 100 equiv of norbornene in the presence of 25 equiv of *p*-methoxystyrene gave a 100-mer with PDI = 1.10.

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Received February 8, 1990
Revised Manuscript Received April 27, 1990

Registry No. Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$, 108969-04-6; *trans*-1,3-pentadiene, 2004-70-8; norbornene (homopolymer), 25038-76-0; styrene, 100-42-5; 2,3-bis(trifluoromethyl)norbornadiene (homopolymer), 72920-56-0.

Monitoring the Molecular Scale Effects of Physical Aging in Polymer Glasses with Fluorescence Probes

Physical aging is described as the gradual approach toward equilibrium of a nonequilibrium amorphous solid below T_g[1] and has been found to affect many properties of or processes in amorphous polymers: volume recovery,[1–4] enthalpy relaxation,[5] dielectric relaxation,[6] tensile modulus and stress relaxation,[7] yield stress,[8] positron annihilation,[9] neutron scattering,[10] X-ray scattering,[11,12] permeation,[13,14] electrical conductivity,[15] and the behavior of spectroscopic labels and probe molecules (electron spin resonance[16] and photochromic[17–19]). Only recently have the effects of physical aging on polymers been studied with fluorescence techniques.[19–21]

Loutfy et al.[22] demonstrated that the fluorescence quantum yields, intensities, and lifetimes of (dialkylamino)benzylidenemalononitriles (DAABMN) are sensitive to viscosity changes in low-viscosity solvents[22c] and follow a WLF free volume relation in high-viscosity media.[22c,g] Sensitivity to glass transitions of polymeric systems was also demonstrated, further suggesting a sensitivity to free volume and mobility.[22b,d,g] These charge transfer probes are viscosity sensitive through rotational nonradiative decay mechanisms from the singlet excited state. Three mechanisms have been identified for these probes: rotation of the donor group,[22,23] rotation of the acceptor group,[22,23] and isomerization around the double bond.[23–25] A decrease in these rotational abilities increases the probability of radiative decay; hence, the fluorescence quantum yield, intensity, and lifetime increase. Therefore, the fluorescence intensity increases with an increase in local viscosity or a decrease in the local mobility or free volume.

We have found that DAABMN probes have the sensitivity to monitor the changes that occur in polystyrene and poly(methyl methacrylate) glasses during physical aging and report the preliminary results in this paper.

Experimental Section. Polystyrene (PS; nominal MW = 575 000; $M_w/M_n \leq 1.06$) and poly(methyl methacrylate) (PMMA; nominal MW = 265 600; $M_w/M_n \leq 1.15$) were used as received from Pressure Chemical. The fluorescence probes used were 4-(diethylamino)benzylidenemalononitrile (DEABMN) and 4-(dimethylamino)benzylidenemalononitrile (DMABMN) (from Molecular Probes).

Films doped with fluorescent probe were cast from 7 wt % polymer solutions in dichloromethane (Aldrich, spectrophotometric grade) onto 2 in. × 2 in. × 1/16 in. quartz slides. After they were dried at ambient temperature and pressure for 24 h, the PS films were dried 1 day under vacuum at 25 °C and an additional 2 days under vacuum at 60 °C to remove residual solvent. PMMA films were dried at ambient temperature and pressure for 1 week before being placed under vacuum at 60 °C for 2 days. PMMA films required additional time at ambient conditions to avoid bubbling during vacuum drying. Dry films contained less than 0.01 wt % probe and were less than 150 μm thick.

0024-9297/90/2223-3536$02.50/0