*Macromolecules* **2001,** *34,* 5370−5372

# Controlled Radical Polymerization of Acrylic Acid in Protic Media

**Catherine Ladavière, Nicole Dörr, and Jérôme P. Claverie***

*LCPP CPE/CNRS 43, Bd 11 Novembre 1918, BP 2077, 69616 Villeurbanne Cedex, France*

*Received February 27, 2001*
*Revised Manuscript Received May 30, 2001*

**Introduction.** Poly(acrylic acid) (PAA) is widely used as scale inhibitor and as dispersant, e.g., for $CaCO_3$.[1] For these uses, it is desirable to prepare narrowly distributed samples, since viscosity and dispersion capacity are drastically influenced by molecular weight distribution (MWD).[2] With controlled radical polymerization, the preparation of monodisperse PAAs (from AA monomer) can be envisioned. Nitroxide-mediated polymerizations of AA are problematic due to nitroxide decomposition in acidic medium.[3] ATRP polymerization is uncontrolled[4] since the polymer can ligate the metal. Using reversible addition fragmentation transfer (RAFT), Rizzardo was the first to describe the controlled polymerization of AA.[5] Albeit that the polydispersity index (PDI) is low (1.23), the polymerization is extremely slow (18% yield in 4 h at 60 °C). According to these authors, this strong retardation originates from the intrinsic stability of the intermediate radical in the fragmentation step (Scheme 1) or the slow reinitiation of the fragmented radical or a specific interaction between the radical and the chain transfer agent (CTA).[6]

Controlling the AA polymerization in aqueous (or alcoholic) medium is especially challenging because the propagation rate constant is extremely high and gel formation is very rapid.[7] For this purpose, we have screened various CTAs suitable for RAFT[5,6,8−10] or for MADIX.[11]

**Experimental Section.** CTA synthesis is reported in the Supporting Information.

MWD values were determined on a GPC equipped with a ultrahydrogel linear 7.8 × 30 column calibrated with 5 PAA standards (Polymer Labs). Elution was performed at 60 °C (0.5 mL/min) using an aqueous buffer ($NaHCO_3$ 0.05 M, $NaNO_3$ 0.1 M, $NEt_3$ 0.02 M, $NaN_3$ 0.03%). To obtain representative results, samples were neither purified nor modified before analysis. For example, consider entry 20 (Table 1): $M_n$(PDI) = 1800 (1.4); after precipitation−redissolution, $M_n$(PDI) = 1900 (1.2); after methylation, $M_n$(PDI) = 2300 (1.1) (GPC, THF, PS standards).

NMR data were acquired on a Bruker DRX 400. The MALDI−TOF instrument (Voyager-DE STR, PerSeptive Biosystems, negative ions detections) used a nitrogen laser (337 nm) and accelerating voltage of 25 kV with external mass calibration (Sequazyme). The MALDI target was prepared by successive addition of matrix solution (1 $\mu$L of 3-$\beta$-indoleacrylic acid in THF, 0.25 M), polymer solution (1 $\mu$L of PAA (20 g/L) acid-form from $H^+$ ion-exchange resin), and THF (1 $\mu$L).

**Polymerization Procedure.** AA, CTA, and solvent were degassed and brought to 90 °C after adding the initiator (4,4′-azobis(4-cyanovaleric acid), V501). The polymerization was stopped by two inhibitors (BHT, Cupferron), and the polymer and monomer were neutralized by an aqueous solution of 10 M NaOH. This also cleaved the dithio-terminated chains. Conversions were determined gravimetrically and by HPLC (integration of the AA peak).

**Table 1. Polymerization of AA in Ethanol Using V501 as Initiator at 90 °C, Where [AA]:[CTA]:[V501] = 50:1:0.1 and [AA] = 2.92 mol/L**

| | CTA | reaction time (min) | convn (%) | $M_n$(theor)[c] | $M_n$(exptl) | PDI |
|---|---|---|---|---|---|---|
| 1 | **1a** | 120 | 15 | 705 | 1000 | 1.4 |
| 2 | **1b** | 120 | 30 | 1410 | 1000 | 1.4 |
| 3 | **1c** | 120 | 10 | 470 | 2700 | 2.1 |
| 4 | **1d** | 120 | 20 | 940 | 900 | 1.3 |
| 5 | **2a** | 120 | >99 | 4700 | 3900 | 3.3 |
| 6 | **2b** | 120 | 95 | 4500 | 3800 | 3.0 |
| 7 | **3a**[a] | 60 | 98 | 4600 | 5000 | 3.4 |
| 8 | **3b** | 120 | 95 | 4470 | 2750 | 1.7 |
| 9 | **3c** | 120 | 30 | 1410 | 1850 | 1.9 |
| 10 | **3d** | 10 | 26 | 1220 | 1200 | 1.9 |
| 11 | **3d** | 20 | 80 | 3800 | 2200 | 1.9 |
| 12 | **3d** | 120 | >99 | 4700 | 2900 | 1.8 |
| 13 | **4a** | 120 | 90 | 3800 | 2400 | 1.8 |
| 14 | **4b** | 10 | 24 | 1200 | 1750 | 1.4 |
| 15 | **4b** | 20 | 39 | 1900 | 2400 | 1.4 |
| 16 | **4b** | 30 | 66 | 3100 | 3800 | 1.3 |
| 17 | **4b** | 60 | 79 | 3700 | 4100 | 1.3 |
| 18 | **4b** | 90 | >99 | 4700 | 4700 | 1.4 |
| 19 | **4c** | 120 | >99 | 4700 | 3650 | 2.3 |
| 20 | **5a** | 120 | >99 | 2350 | 1800 | 1.4 |
| 21 | **5a** | 10 | 7 | 175 | 850 | 1.3 |
| 22 | **5a** | 20 | 40 | 940 | 1150 | 1.4 |
| 23 | **5a** | 30 | 66 | 1550 | 1450 | 1.4 |
| 24 | **5a** | 90 | >99 | 2350 | 1800 | 1.4 |
| 25 | **5b**[b] | 90 | 96 | 4600 | 2850 | 1.4 |

[a] [AA]:[**3a**]:[V501] = 67:1:0.13. [b] [AA]:[**5b**]:[V501] = 100: 1:0.1. [c] Using 94 as monomer molecular weight, as GPC eluant is basic.

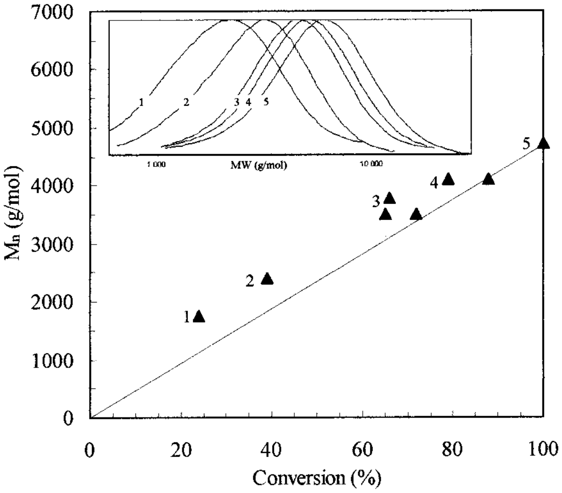


**Figure 1.** $M_n$ vs conversion with CTA (**4b**): (▲) experimental $M_n$; (plain line) theoretical $M_n$. Points 1−5 correspond to entries 14−18 in Table 1.

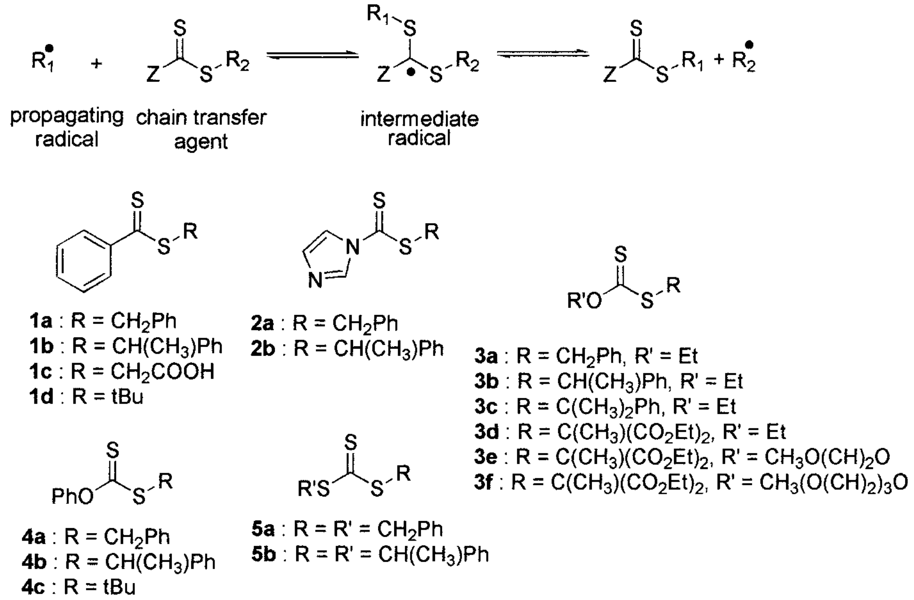
NMR. PAA **5a** ($^1H$, $D_2O$): 7.4−7.2 (5H, $C_6\mathbf{H}_5$), 2.3−1.9 (27H, $C\mathbf{H}CO_2Na$), 1.8−1.3 (54H, $C\mathbf{H}_2$), $M_n$(NMR) = 2550. ($^{13}C$, $D_2O$): 185 ($\mathbf{C}O_2Na$), 143−126 ($\mathbf{C}_6H_5$), 47−45 ($\mathbf{C}HCO_2Na$), 39−35 ($\mathbf{C}H_2$). **5b** ($^1H$, $D_2O$): 7.4−7.2 (5H, $C_6\mathbf{H}_5$), 2.3−1.9 (47H, $C\mathbf{H}CO_2Na$), 1.8−1.3 (94H, $C\mathbf{H}_2$), 1.3−1.2 (3H, $C\mathbf{H}_3$) $M_n$(NMR) = 4400. **3d** ($^1H$,

---

* To whom correspondence should be addressed. E-mail: claverie@flamel.com. Telephone: (33)472783434. Fax: (33)472783-435.

10.1021/ma010358v CCC: $20.00

**Scheme 1. Addition Fragmentation Equilibrium between Propagating Radicals and Dormant Chains**



$D_2O$): 2.3–1.9 (44H, C**H**$CO_2H$), *1.8*-1.3 (88H, C**H**$_2$), *1.8* (3H, C**H**$_3$), $M_n$(NMR) = 4150.

**Results and Discussion.** In RAFT, the control over the polymerization is strongly influenced by the choice of the substituents Z and R in the CTA structure (Scheme 1).[6,8–10] For efficient transfer and control, R should be a good free-radical leaving group, i.e., a more stable radical than the incoming propagating radical. For AA, R should therefore be at least a secondary carbon bearing one stabilizing substituent (α-carbonyl, α-phenyl). Z should be able to stabilize the intermediate radical, so that the energy barrier between reactants and intermediate radical (Scheme 1) is low enough. Aryl and thiol groups are suitable for Z whereas dialkylamino (especially when the nitrogen atom is $sp^3$) and alkoxy groups are less adequate.[6,8–11]

We observe (Table 1) a correlation between stability of the intermediate radical, decrease of the polymerization rate and efficiency of control. At 90 °C, under conditions described in Table 1, the uncontrolled polymerization of AA is quantitative in less than 10 min (cross-linked polymer, $M_n$(soluble) = 33 100, PDI = 4.3),

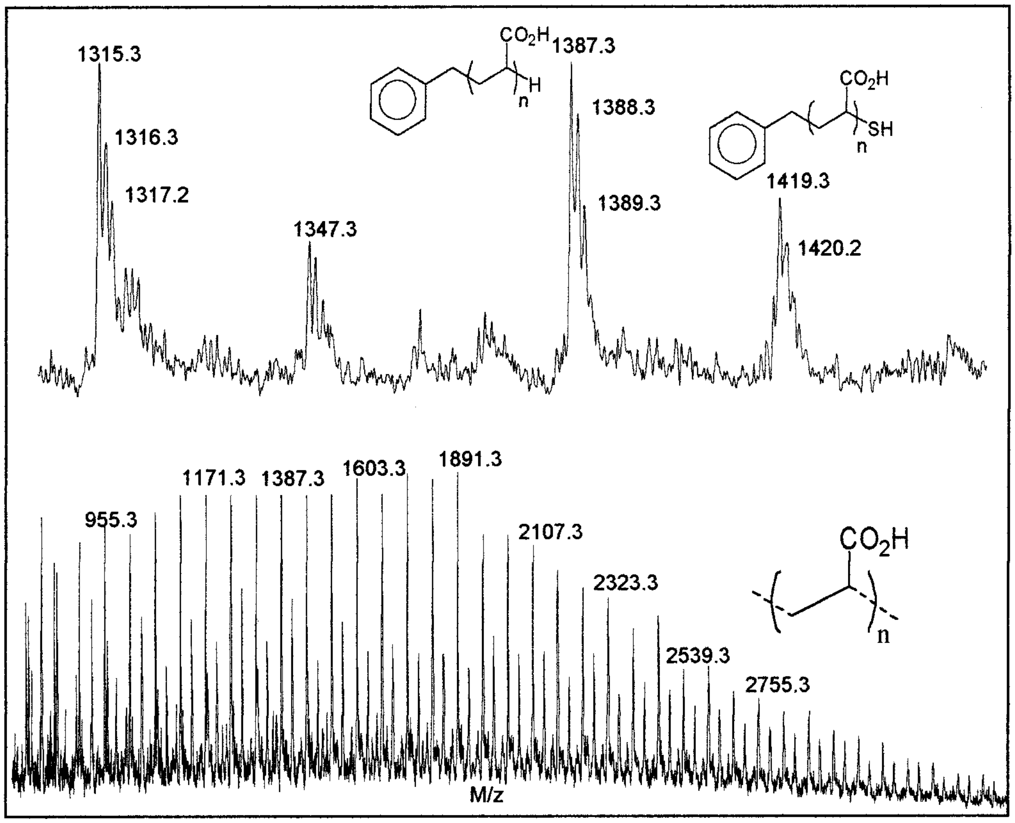


**Figure 2.** Negative-ion MALDI–TOF mass spectrum of PAA synthesized with **5a** (entry 20 in Table 1). The polymer is treated with acid ion-exchanging resin prior analysis.

contrasting with 36% conversion in 8 h for **1b**. Control is improving in the direction **3** < **4** < **5** < **1**, also corresponding to the predicted stability of the intermediate radical (RO < PhO < RS < Ph). For dithiocarbamates **2**, we observe that dithiocarbamates readily react with solvent (water or ethanol) at 80 °C, yielding decomposed CTAs, resulting in the absence of control.

The influence of the leaving group R is also obeying the predicted trend: control is improving for more and more stabilized leaving groups (**3a** < **3b** < **3c** or **5a** < **5b**). With a poor homolytic leaving group, the productive transfer between propagating radical and CTA is a rare event: dormant chains are not all created together, resulting in disperse MWD (**3a**).

Linear increase of $M_n$ vs conversion is observed for the most potent CTAs such as **3c**, **3d**, and **4b** (Figure 1), **5a** and **5b**. For **4b**, the experimental molecular weight matches the theoretical one, except at very low conversion, where the molecular weight is comprised between 0 and 500. Extrapolated value at 0 conversion gives access to $C_{tr}$ of the CTAs (first transfer, not the exchange of dormant chains).[13,14] For compounds **3c, 3d**, **4b, 5a** and **5b,** $C_{tr}$ is respectively equal to 1.4, 6.8, 5, 3, and 24.

Aqueous polymerizations can be carried out with CTAs **3d**, **3e**, and **3f**. **3d** (respectively, **3e** and **3f**) is soluble in a 44:56 (w/w) (40:60, 33:77) AA–water mixture. In all cases, polymerizations are quantitative in less than 10 min, yielding low molecular weight polymers ($M_n = 3500$ for **3d**, 3400 for **3e**, and 3200 for **3f**) with PDIs less than 1.9. For **3d**, in methanol, ethanol, or 2-propanol, polymers have similar characteristics (PDI = 1.9 in methanol, 1.8 in ethanol and 1.9 in 2-propanol). As expected, kinetics are strongly affected by the solvent nature: water $\gg$ 2-propanol $\sim$ ethanol > methanol.

After treatment with NaOH, polymers are analyzed by MALDI–TOF and $^1$H NMR. In the MALDI–TOF mass spectrum (Figure 2), separate oligomers are clearly resolved, showing two distinct families separated by 32 $m/z$. In the same family, the difference between peaks is 72 $m/z$ corresponding to AA. The minor family corresponds to expected product, where one extremity is R group (benzyl for **5a**) and the other is SH (product of the xanthate/trithiocarbonate cleavage with NaOH).[12] The major family corresponds to the product which is R- and H-ended. We assume that an H atom transfer reaction with solvent has occurred (possibly during the treatment with NaOH) as described for xanthates.[15] It can also possibly arise from termination reactions by disproportionation (very unlikely as no double bonds observed by NMR) or by transfer to polymer. Coupling products and diazo-initiated chains are not observed. An identical pattern is observed with polymers produced with **5b** ($PhCH(CH_3)-(AA)_n-H$: $m/z = 106 + 72n$) and **3d** ($CH(CH_3)CO_2H-(AA)_n-H$: $m/z = 74 + 72n$, where saponification and subsequent decarboxylation has occurred upon treatment with NaOH). End group identification by NMR confirmed the MALDI–TOF observation (see experimental results).

To conclude, polymerization of AA was found to be controlled in alcohol and water, especially with phenoxyxanthates **4** or with trithiocarbonates **5**. As expected for a controlled radical polymerization, linear increase of molecular weight vs conversion and moderate PDIs were obtained. The use of these polymers as dispersing agent will be disclosed in a further communication.

**Acknowledgment.** We thank COATEX, and especially J. M. Suau and J. B. Egraz, for financial and scientific support and M. Llauro, F. Delolme, and G. Dessalces for MALDI–TOF and NMR.

**Supporting Information Available:** Text giving experimental details on the synthesis of compounds **2a**, **2b**, **3a**, **3c**, **3d**, **3e**, **3f**, **4a**, **4b**, **4c**, and **5b** and figures showing their structures. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Buchholz, F. L. *Ullmann's Encyclopedia of Industrial Chemistry*; Hawkins, S., Schulz, G., Eds.; VCH: Weinheim, Germany, 1992; Vol. A21, pp 143–156.

(2) Bonnet, C.; Mongoin, J.; Ravet, G.; Suau, J. M. French Patent, FR2655875 Coatex, 1991.

(3) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904–3920.

(4) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901–915.

(5) Chiefari, J.; Chong, B. Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.

(6) Hawthorne, D. G.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 5457. Moad, G.; Chiefari, J.; Krstina, J.; Postma, A.; Mayadunne, R. T. A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 933–1001. Retardation is also discussed in: Monteiro, M. J.; de Brouwer, H. *Macromolecules* **2001**, *34*, 349–352.

(7) Kuchta, F. D.; Herk, A. L. V.; German, A. N. *Macromolecules* **2000**, *33*, 3641.

(8) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. *Macromolecules* **2000**, *33*, 243.

(9) Chiefari, J.; Jeffery, J.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 7700.

(10) Chong, B. Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071.

(11) Corpart, P.; Charmot, D.; Biadatti, T.; Zard, S.; Michelet, D. French Patent FR 2773161 1997.

(12) Rizzardo, E.; Chiefari, J.; Chong, B. Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Thang, S. H. *Macromol. Symp.* **1999**, *143*, 291.

(13) Farcet, C.; Lansalot, M.; Pirri, R.; Vairon, J. P.; Charleux, B. *Macromol. Rapid. Commun.* **2000**, *21*, 921.

(14) Uzulina, I.; Kanagasabapathy, S.; Claverie, J. *Macromol. Symp.* **2000**, *150*, 33.

(15) Quiclet-Sire, B.; Zard, S. *J. Am. Chem. Soc.* **1996**, *118*, 9190.

MA010358V