Conversion-Dependent Molecular Weight of the Polymer in Free Radical Polymerization of Captodative Substituted (Acyloxy)acrylates

Hitoshi Tanaka,* Yasushi Kunouchi, and Tomomi Takeichi

Department of Optical Science and Technology, Faculty of Engineering, Tokushima University, 2-1 Minamijosanjima, Tokushima 770, Japan

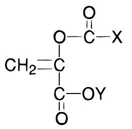
Received February 19, 1997; Revised Manuscript Received April 25, 1997[⊗]

ABSTRACT: The radical homopolymerization of captodatively substituted methyl α-acetoxyacrylate (MAA) is studied by comparing it with that of the α-trifluoroacetoxy, the α-butyryloxy, and the ethyl ester analogs at 40 °C. The yield of the polymer is much influenced by the acyloxy substituents, and the polymer molecular weight increases with conversion in bulk MAA and ethyl ester polymerizations in contrast to other polymerizations. Dilution of the MAA polymerization system, however, results in no increase in the polymer molecular weight during the polymerization. Some polymer−polymer interactions between captive and dative moieties in MAA polymer are discussed on the basis of the measurement of the viscosity of the polymerization system and the polymer solution.

Introduction

Molecular weight controlled radical polymerization has attracted much attention in connection with living or pseudoliving radical polymerizations. New initiating systems recently developed describe useful ways to achieve chemically controlled radical polymerization. Atom transfer radical polymerization (ATRP),[1] nitroxide-mediated stable free radical polymerization (SFRP),[2] and the polymerization using iniferter (initiator−transfer−terminator reagent)[3] are well-known examples. Molecular weight has also been controlled physically in polymerization systems including polymerization in intercalation compounds,[4] inclusion polymerization,[5] and template polymerization.[6]

Recently, we reported[7] that captodatively (cd) substituted (geminal substitution of both electron-withdrawing (captive) and electron-donating (dative) groups on the same atom)[8] acrylates such as methyl α-acetoxyacrylate (MAA) undergo a unique polymerization to give a polymer in moderate yield in spite of the cd character of the monomer. That is, we found that the synergistic and asymmetric polarization of the cd monomer affected the polymerization rate, in particular propagation and termination rates. In this paper, we want to demonstrate the increase in polymer molecular weight with conversion even in the initial stage of the free radical polymerization in homogeneous solution by using cd olefins.



MAA: X=CH_3, Y=CH_3
MBA: X=n-C_3H_7, Y=CH_3
MTFAA: X=CF_3, Y=CH_3
EAA: X=CH_3, Y=C_2H_5

Experimental Section

Materials. MAA[9] and methyl (α-butyryloxy)acrylate (MBA)[10] were synthesized according to the methods in previous papers. Ethyl α-acetoxyacrylate (EAA) was prepared by the reaction of ethyl pyruvate and acetic anhydride in the presence of *p*-toluenesulfonate for 16 h at 120 °C according to the literature.[11] Methyl (α-trifluoroacetoxy)acrylate (MTFAA) was synthesized by the reaction of methyl pyruvate and trifluoroacetic anhydride in dichloromethane by slowly adding triethylamine to the mixture according to the procedure for the ethyl ester analogue.[12] Bp (°C/mmHg): MAA, 64−65/8 (64−65/8);[9] MBA, 60/4 (60−61/4);[8] MTFAA, 55−56/30; EAA, 62/3 (99−100/35).[13] ^{1}H-NMR ($CDCl_3$, ppm): MTFAA, 3.87 (s, 3H), 5.74 (d, $J = 2.8$ Hz, 1H), 6.26 (d, $J = 2.8$ Hz, 1H); EAA, 1.31 (t, $J = 7.0$ Hz, 3H), 2.21 (s, 3H), 4.26 (q, $J = 7.0$ Hz, 2H), 5.47 (d, $J = 1.8$ Hz, 1H), 6.03 (d, $J = 1.8$ Hz, 1H). Anal. Calcd for $C_6F_3H_5O_4$ (MTFAA): C, 36.38; H, 2.54. Found: C, 36.25; H, 2.83. Calcd for $C_7H_{10}O_4$ (EAA): C, 53.16; H, 6.37. Found: C, 52.88; H, 6.12.

Commercially available (Wako Chemicals) 2,2′-azobisisobutyronitrile (AIBN) and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) were used after recrystallization from ethanol and toluene respectively. Vinyl acetate and methyl methacrylate were purified by fractional distillation.

Polymerization. Polymerizations were generally carried out in a sealed ampule with shaking at the given temperature. The ampule which contained the required amounts of reagents was degassed several times by a freeze−thaw method and then sealed under vacuum and placed in a constant temperature bath. The resulting polymer was isolated by pouring the contents of the ampule into a large amount of ethanol for vinyl acetate polymerization and into methanol for other polymerizations. The polymer sample used for the size exclusion chromatograph (SEC) measurement was prepared by sealing the degassed ampule under argon gas, and it was taken directly from the polymerization mixture by using a microsyringe. The sample (polymerization mixture) taken was diluted with SEC solvents such as dichloromethane or tetrahydrofuran to 0.1% concentration, and it was injected into a SEC column. Conversion of the monomer in the polymerization was determined by calibrating the consumption of the monomer by means of gas chromatography using a biphenyl as a standard sample.

Measurement. Viscosity of the polymerization system was measured directly by stopping the polymerization with hydroquinone after opening the sealed polymerization ampule. An Ubbelhode viscometer was used for its measurement at 40 °C. The plot of the concentration (C) of MAA polymer solution against the specific viscosity (η_{sp}) was carried out in dichloromethane at 30 °C. ^{1}H-NMR spectra were measured on a JEOL JNM-EX400 (400 MHz) spectrometer. Number- and weight-average molecular weights (M_n and M_w) of the polymer were determined by SEC using a Tosoh HLC-8020 (columns: TSKgel-G7000HHR + G5000HHR + G5000HHR or G3000HHR) in dichloromethane for poly(MAA), poly(MBA), and poly(EAA) or a Toyosoda HLC-802A (columns: TSKgel-G7000HLX + G5000HLX + G5000LX) in tetrahydrofuran for poly(MTFAA) and poly(vinyl acetate) based on a standard polystyrene at 35 °C.

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

S0024-9297(97)00225-8 CCC: $14.00

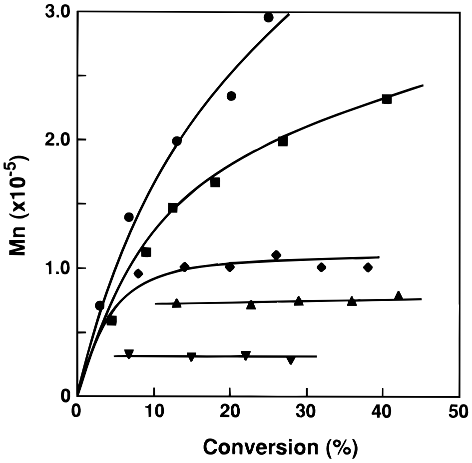


Figure 1. Dependence of polymer molecular weight on conversion for the polymerization of MAA by V-70 at 40 °C. [MAA] = bulk (●), 7.0 (■), 5.1 (◆), 3.9 (▲), and 2.6 (▼) mol/L; [V-70] = 6.7 × 10^{-3} mol/L.

Results and Discussion

The polymerizations of the acyloxyacrylates and methyl methacrylate were carried out in bulk for 8 h by using AIBN ([AIBN] = 5.0 × 10^{-3} mol/L) at 60 °C. The polymer yields were determined to be 79.3, 21.6, and 81.0% for EAA, MTFAA, and methyl methacrylate polymerizations, respectively. MAA and MBA gave polymers in 69.4 and 18.2% yield, respectively, under the same conditions.[7] This suggests that the polymer yield is much influenced by the acyloxy substituents.

Figure 1 shows the relationship between the conversion and the molecular weight of the polymers produced during the radical polymerization of MAA initiated by V-70 at 40 °C. It is noted that in the bulk state the molecular weight of MAA polymer increases with conversion even in the initial stage of the polymerization. This increasing tendency is reduced gradually by dilution as seen in this figure, and polymerization at concentrations as high as [MAA] = 3.0 mol/L results in invariant M_n values over a wide range of conversion as often observed in conventional radical polymerization.

The maximum peaks in SEC curves from samples taken directly from the MAA polymerization mixture ([MAA] = 7.0 mol/L) shift clearly to the higher molecular weight region, but the polymer obtained at higher conversion seems to contain at least partially the polymer produced at lower conversion and is actually observed as a small shoulder in the low molecular weight region in Figure 2A. Indeed, the molecular weight distribution (M_w/M_n) of MAA polymer in Figure 2 increases gradually from 1.67 to 1.94 with conversion, supporting an inclusion of component C in polymer A in Figure 2. Similar increases in M_w/M_n were also observed in bulk MAA polymerization; i.e. M_w/M_n increases little by little from 1.47 to 1.56, 1.99, and 2.05 at 3, 7, 13, and 16% conversion, respectively. This implies that the polymer produced in the initial stage of the polymerization mostly remains as a dead polymer that does not grow anymore, in contrast to a living anionic polymerization[14] in which the anionic species generated in the initial stage can propagate to a long chain polymer anion and is still alive even at the final stage of the polymerization to give a monodispersed polymer.

Such an increase in polymer molecular weight has been well-known in a high viscosity medium as a gel effect even in a radical polymerization,[15] in which termination depends on the diffusion of each polymer chain, i.e. diffusion control, to reduce a termination. In the bulk MAA polymerization system, viscosity (η_{rel}) values for the medium were measured to be 1.08 and 1.22 at 3.0 and 7.0% conversions, respectively. From this the M_n value is calculated to be 8.3 × 10^4 at 7.0% conversion according to the equation $M_n/\eta_{rel}^{0.5}$ = constant.[16] Large deviation of the measured M_n (=1.4 × 10^5) from the calculated one (=8.3 × 10^4) suggests that the increase in the molecular weight during the polymerization cannot be explained adequately just by the depression of termination due to the increase in viscosity.

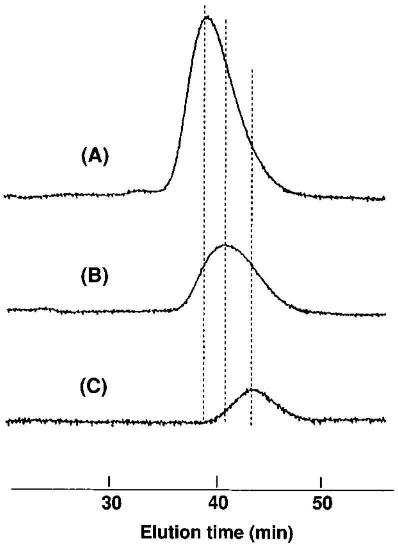


Figure 2. SEC curves of the polymer produced during the polymerization of MAA by V-70 in dichloromethane at 40 °C in conversions of 17 (A), 8 (B), and 4 (C) %. [MAA] = 7.0 mol/L; [V-70] = 6.7 × 10^{-3} mol/L.

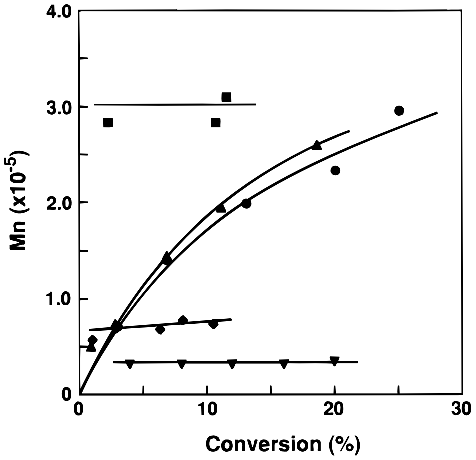


Figure 3. Dependence of polymer molecular weight on conversion for the polymerizations of MAA (●), MBA (■), MTFAA (◆), EAA (▲), and vinyl acetate (▼) by V-70 at 40 °C. [V-70] = 6.7 × 10^{-3} mol/L.

A similar increasing curve is also observed in the polymerization of EAA under the same conditions as in the case of MAA as shown in Figure 3. The polymerization of MBA and MTFAA, however, represents no increase in polymer molecular weight with conversion in the initial stage of the polymerization, as is generally known. In addition, the small or singly captive or dative substituted olefins including methyl methacrylate and vinyl acetate also show no increase in molecular weight at least up to 20% conversion as already known[17] and seen in Figure 3, respectively. These results suggest

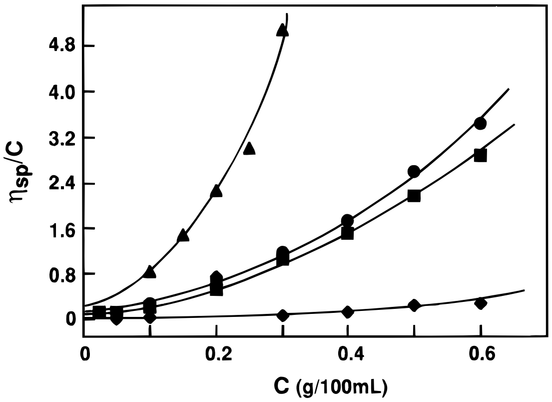


Figure 4. Relationship between the concentration of MAA polymer (*C*) and the specific viscosity (η_{sp}) of the polymer in dichloromethane at 30 °C. $M_n = 1.15 \times 10^6$ (▲), 8.12×10^5 (●), 5.37×10^5 (■), and 1.53×10^5 (◆).

that some synergistic dipole–dipole interaction between captive and dative moieties of MAA and EAA monomers and polymers seems to play an important role, not only in the termination but also in other elemental reaction processes, including the propagation. It has been reported that the polarity of styrene derivatives affects the copolymerization reactivity[18] and also the homopolymerization rate[19] even in a radical mechanism. However, there is little work concerning the dependence of the molecular weight on monomer polarity in the field of normal radical polymerization in a homogeneous solution. The lack of such strong interaction in the case of MTFAA, because of the less electron-donating (less cd polarization) power of the trifluoroacetoxy moiety, therefore, brings about a normal radical polymerization reaction. The bulkiness of the butyryloxy moiety in MBA monomer also induces a normal polymerization as seen in Figure 3.

To demonstrate the polymer–polymer interaction, the viscosity of the MAA polymer solution was measured as a function of the polymer concentration. As shown in Figure 4, such a plot would not give a straight line, and the increase in the curves accelerates with increasing concentration of the polymer solution. However, in dilute medium the viscosities decrease in an accelerated manner, and the intrinsic viscosities are fairly low considering their molecular weights. This may support some particular dipole–dipole intermolecular and intramolecular interaction between the polymer chains in high and low concentrations of the polymer, respectively. Chapiro and his associates have observed a fast propagation in acrylonitrile polymerization[20] and autoacceleration of acrylic acid polymerization[21] because of a matrix effect due to dipolar–dipolar association. A similar effect has also been found in a binary system;[22] i.e., the polymerization rate of N-vinylimidazole can be further enhanced by using a poly(methacrylic acid) template and the molecular weights of the polymers formed by template polymerization are up to 70 times higher than those of polymers produced in the absence of the template and also higher than the molecular weights of the templates themselves although such an effect seems to depend on the conditions.[23] These have been explained in a satisfactory manner by the microscopic side chain interaction between adsorbed mobile monomer and template-associated radicals or polymer chains formed in the early stage of the polymerization. Similar side chain interactions between captive and dative moieties may also take place in MAA polymerization. A more detailed study is now in progress.

Conclusions

It has been believed that the molecular weight of the polymer produced during a homogeneous radical polymerization in bulk is not changed in the initial stage of the polymerization except in special cases such as matrix polymerizations. Captodatively substituted MAA and its ethyl ester analogue, however, were found to undergo a molecular weight increased radical polymerization depending on conversion in the bulk state. From the kinetic study of MAA radical polymerization,[7] it has been speculated that the synergistic and asymmetric polarization of the monomer can affect the polymerization process, in particular propagation and termination reactions. Such a polarization effect also seems to play an important role in the molecular weight increased polymerization studied.

References and Notes

(1) Greszta, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 638.
(2) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1993**, *2*, 66.
(3) Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127.
(4) Tanaka, H.; Kameshima, T.; Sato, T.; Ota, T. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 229.
(5) Harada, A.; Li, J.; Kamachi, M. *Nature* **1992**, *356*, 325.
(6) Tan, Y. Y.; Ekenstein, G. O. R. A. *Macromolecules* **1991**, *24*, 1641.
(7) Tanaka, H.; Yoshida, S. *Macromolecules* **1995**, *28*, 8117.
(8) Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148.
(9) Tanaka, H.; Sakai, I.; Sasai, K.; Sato, T.; Ota, T. *J. Polym. Sci., Polym. Lett.* **1988**, *26*, 11.
(10) Bessiere, J.-M.; Boutevin, B.; Bachire, A.; Harfi, A. *Makromol. Chem.* **1993**, *194*, 2939.
(11) Wolinsky, J.; Novak, R.; Vasileff, R. *J. Org. Chem.* **1964**, *29*, 3596.
(12) Barton, D. H. R.; Chern, C.-Y.; Jaszberenyi, J. Cs. *Tetrahedron* **1995**, *51*, 1867.
(13) Thomas, M. L.; Unruh, C. C. *Ind. Eng. Chem.* **1958**, *50*, 1119.
(14) Szwarc, M. *J. Am. Chem. Soc.* **1956**, *78*, 2656.
(15) Schulz, G. V.; Harborth, G. *Makromol. Chem.* **1947**, *1*, 106.
(16) Kobatake, S.; Yamada, B. *Macromolecules* **1995**, *28*, 4047.
(17) Norrish, R.; Smith, R. *Nature* **1942**, *15*, 336.
(18) Imoto, M.; Kinoshita, M.; Nishigaki, M. *Makromol. Chem.* **1966**, *94*, 238.
(19) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 5748.
(20) Burillo, G.; Chapiro, A.; Mankowski, Z. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 327.
(21) Chapiro, A.; Dulieu, J. *Eur. Polym. J.* **1977**, *13*, 563.
(22) Van de Grampel, H. T.; Tan, Y. Y.; Challa, G. *Macromolecules* **1990**, *23*, 5209.
(23) Ferguson, J.; Al-Alawi, S.; Granmayeh, R. *Eur. Polym. J.* **1983**, *19*, 475.

MA9702253