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Chain transfer activity of some activated allylic compounds

Gordon F. Meijs, Ezio Rizzardo*, and San H. Thang

CSIRO Division of Chemicals and Polymers, Private Bag 10, Clayton Vic. 3168, Australia

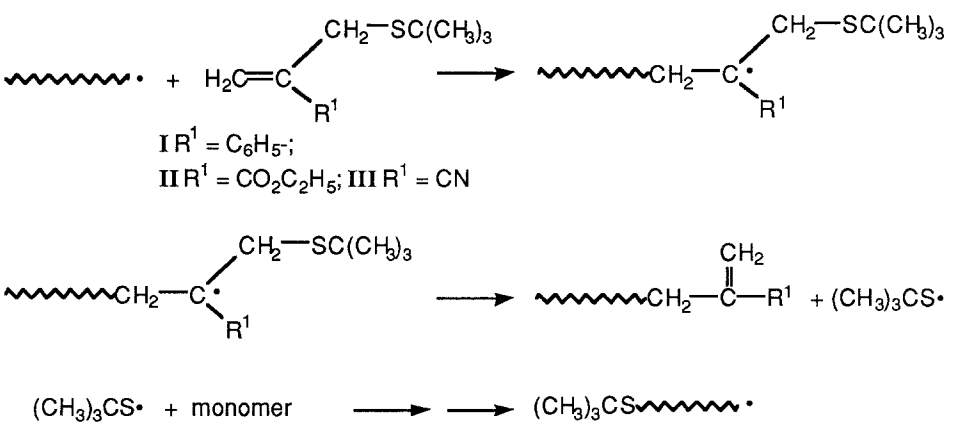
Summary

Various olefins that are activated towards free radical addition and contain a homolytic leaving group in the allylic position are effective chain transfer agents in free radical polymerizations of methyl methacrylate and other monomers. These allylic compounds include bromides, phosphonates, stannanes, thioethers, sulfoxides, and sulfones. Allylic silanes and chlorides, however, do not posess significant chain transfer activity. Suitable activating substituents towards radical addition are phenyl, ethoxycarbonyl, cyano, and acetoxy. Several of the compounds have an advantage over thiols in that they do not contain sulfur.

Introduction

We have recently reported that the allylic *tert*-butyl sufides **I-III**, activated by phenyl, ethoxycarbonyl or cyano groups, respectively, are efficient chain transfer agents in the free radical polymerization of methyl methacrylate and styrene (1,2). The lowering of molecular weight in polymerizations carried out in the presence of **I-III** is consistent with a mechanism that contains both radical addition and fragmentation steps (Scheme 1).

Scheme 1:



The effectiveness of compounds **I-III** in chain transfer reactions can be rationalized in terms of the activation towards radical addition of the double bond by phenyl, ethoxycarbonyl or cyano substituents, and the presence of a weak bond (the carbon-sulfur bond) in a β-position to the adduct radical that can undergo fragmentation (the second equation in Scheme 1). The ease with which radicals with a β sulfur substituent fragment has previously been established in studies by Barton and Crich (3) and Keck and Byers (4). We now report

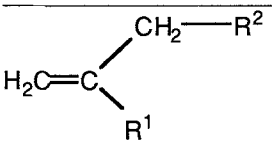
*To whom offprint requests should be sent

further examples of allylic compounds that show activity in lowering molecular weight in free radical polymerizations. This study was undertaken as part of a search for new examples of the addition-fragmentation type of chain transfer reaction (2) and partly to develop chain transfer reagents that do not lead to undesirable sulfur residues in the resulting polymer.

Results and Discussion

The compounds **IV-XV** shown in Table 1 were synthesised and tested for efficiency in polymerizations of methyl methacrylate initiated with azobisisobutyronitrile at 60 °C. Some of the compounds were also examined in polymerizations of methyl acrylate or styrene; in addition, vinyl acetate was polymerized in the presence of **XV**. The chain transfer constants were calculated from molecular weight data obtained by GPC on polymerizations taken to low conversions. The polymerizations were typically carried out with four concentrations of a given chain transfer agent, and the chain transfer constants that appear in Table 1 were obtained from the gradients of graphs of $1/\overline{P}_n$ vs the relative concentrations of the chain transfer agents and monomers.

Table 1. Chain transfer constants at 60 °C



Structure no.	R^1	R^2	MMA	St	MA	VA
IV	CN	Br	2.22		3.00	
V	CN	Cl	0.0075		0.046	
VI	H	Br	0.004			
VII	COOEt	Br	1.45		2.33	
VIII	Ph	Br	2.27	2.93	5.25	
IX	Ph	$P(O)(OC_2H_5)_2$	0.35			
X	Ph	$S(O)(CH_2)_3CH_3$	1.89			
XI	Ph	$S(CH_2)_3CH_3$	1.10	0.68		
XII	COOEt	$Sn(n\text{-}Bu)_3$	3.01			
XIII	COOEt	$Si(CH_3)_3$	0.08			
XIV	COOEt	$S(O)_2Ph$	1.14	5.75		
XV	$OC(O)CH_3$	$S(O)_2Ph$	0.065	0.02	0.20	2.80

The effectiveness of the allylic bromide **IV** in lowering molecular weight in both methyl methacrylate ($C_x = 2.22$) and methyl acrylate ($C_x = 3.00$) polymerizations contrasts with its chlorine analogue **V** and probably reflects the poorer ability of the radical derived from addition to **V** to fragment due to the greater strength of carbon-chlorine bonds. It is noteworthy that the substituted allylic bromide **IV**, which is activated towards the radical addition outlined in Scheme 1, was a substantially better chain transfer agent than its unactivated analogue, allyl bromide **VI** ($C_x = 0.04$ for methyl methacrylate). This observation gives support to the proposal that **IV** undergoes chain transfer by an addition-fragmentation pathway. Although there was a mild retardation of the polymerization of methyl methacrylate in the presence of **IV** (there was an approximate halving of the rate for a 75 fold drop in molecular weight), the mechanism was clearly one that predominantly involved true chain *transfer*, rather than chain termination without efficient reinitiation.

The bromoacrylate **VII** and the styrene derivative **VIII** also displayed activity in chain transfer reactions (see Table 1). The slightly higher chain transfer constant of the styrene derivative **VIII** in polymerizations of methyl methacrylate probably reflects the greater reactivity of styryl compounds toward poly(methyl methacryl)yl macroradicals (as is

suggested by reactivity ratios of the respective monomers). Hence, the addition step of Scheme 1 would be faster and, assuming that this is the crucial step for this material, the chain transfer constant would be greater. Both **VII** and **VIII** did not retard the polymerization to any significant extent.

The phosphonate **IX** showed some chain transfer activity in methyl methacrylate polymerizations; this was consistent with the fact that carbon-phosphorus bonds of this type are relatively weak (5). The radical formed by addition of the propagating poly(methyl methacryl)yl radical to **IX**, therefore, was anticipated to fragment readily. However, in this case, the chain transfer appeared to be mainly degradative, since there was substantial retardation of the polymerization. For example, when sufficient of the chain transfer agent was added to lower the molecular weight of poly(methyl methacrylate) by 2.4 times, the conversion of the polymerization dropped to about 30% of that of the unregulated polymerization. Thus, it was apparent that it is the chain reinitiation part of the process that was inefficient.

There is some indication in the literature (6,7) that carbon-sulfoxide bonds are relatively weak and that sulfinyl radicals are satisfactory homolytic leaving groups. Accordingly, we prepared the sulfoxide **X** and determined that it was effective in lowering molecular weight in methyl methacrylate polymerizations (C_x = 1.9). The polymerization, however, was also retarded. It has been reported that sulfinyl radicals are more stable than their thiyl and sulfonyl radical counterparts (6,7) and that addition products with several olefins, including styrene, cannot be obtained (6) because of reversibility. It appears that the stability of the sulfinyl radical derived from **X** is sufficiently high that reinitiation of polymerization is not favourable. It is noteworthy that the thioether analogue of **X**, structure **XI**, was an effective chain transfer agent with comparable activity to **I**, and did not significantly retard polymerizations of methyl methacrylate or styrene.

Baldwin and coworkers (8) have shown that the the allylic stannane **XII** undergoes facile bimolecular homolytic substitution reactions (S_H2' reactions) which are similar in mechanism to Scheme 1. The experiment reported in Table 1 shows that the stannane **XII** also is active as a chain transfer agent with methyl methacrylate. Evidently, tributyltin radical is a relatively efficient reinitiator of methyl methacrylate polymerizations, because there is little retardation associated with this reagent.

The allylic silane **XIII** was shown to be a poor chain transfer agent for methyl methacrylate; this fact accords with the observations of Hershberger and coworkers (9) that because of the high carbon-silicon bond strength, fragmentation is not favorable.

The two sulfones **XIV** and **XV** exhibited chain transfer activity, although the latter compound, in which the double bond was activated by an acetate substituent, had relatively low chain transfer constants with methyl methacrylate, styrene and methyl acrylate. It was, however, quite reactive towards vinyl acetate. It is likely that the activity of these two compounds is controlled by the rate of the addition step, which is slow in the case of the macroradicals derived from the former three monomers. There was no retardation of polymerization with either of these two compounds, except in the case of **XV** with vinyl acetate, where retardation was a major pathway; our experiments show that sulfonyl radicals are sufficiently reactive to reinitiate chains of polystyrene and poly(methyl methacrylate), but insufficiently reactive to reinitiate chains of poly(vinyl acetate) effectively.

The above results highlight the efficiency of the bromocompounds **IV**, **VII**, **VIII**, and the stannane **XII** as sulfur-free chain transfer agents for free radical polymerizations.

Experimental Section

Procedure for carrying out polymerizations

Azobisisobutyronitrile (34.9 mg) was dissolved in freshly distilled styrene (25 ml). Aliquots (5.0 ml) were removed and added to ampoules containing various amounts of the chain transfer agent. Generally, for a given chain transfer agent/monomer combination, polymerizations were carried out with four different concentrations of the chain transfer agent. The mixtures were then degassed by three freeze-evacuate-thaw cycles and sealed under vacuum (10^{-3} Torr). After the polymerization, the contents of the ampoules were poured into methanol and the precipitated polymers were collected and dried *in vacuo* overnight. A small

portion of each polymer was examined by gel permeation chromatography (GPC) using a Waters Instrument connected to six μ-Styragel columns (10^6, 10^5, 10^4, 10^3, 500, and 100 Å pore size). Tetrahydrofuran was used as the eluent at a flow rate of 1 ml/min and the system was calibrated using narrow distribution polystyrene standards (Waters).

Polymerizations of methyl methacrylate were carried out similarly for 1 h at 60 °C. Azobisisobutyronitrile (48.2 mg) was dissolved in freshly distilled methyl methacrylate (25 ml). Aliquots (2.0 ml) were removed and added to ampoules containing weighed amounts of the chain transfer agent. After the polymerization, the contents of the ampoules were then poured into hexane and the precipitated polymers were collected, dried, and examined as before.

Polymerizations of methyl acrylate were carried out using a stock solution prepared from azobisisobutyronitrile (9.1 mg) and freshly distilled methyl acrylate (25 ml). Aliquots (2.0 ml) were removed and added to ampoules containing thiophene-free benzene (8.0 ml) and weighed amounts of the chain transfer agent. After degassing, the mixtures were polymerized at 60 °C for 1 h. The volatiles were then removed and the polymers were dried in vacuo to constant weight and examined by GPC.

α–(Bromomethyl)acrylonitrile (**IV**)

This compound was prepared using a similar procedure to that described by Villieras and Rambaud (10) for the preparation of ethyl α-(bromomethyl)acrylate. α-(Hydroxymethyl)acrylonitrile (8 g) was added dropwise to phosphorous tribromide (12 g) in dry ether (90 ml) at -10 °C. After the addition, the temperature was allowed to rise to 20 °C and stirring was continued for 3h. The mixture was then cooled to -10 °C and ice water (150 ml) was added in small portions. The mixture was then extracted three times with hexane, washed with brine, dried and distilled to afford α-(bromomethyl)acrylonitrile (4 g, 29%), bp 45-47 °C (2 mmHg). ^{1}H NMR spectrum: ($CDCl_3$) δ 3.85 (2H, br s), 5.95 (2H, m).

α-(Chloromethyl)acrylonitrile (**V**)

This compound was prepared from α-(hydroxymethyl)acrylonitrile and thionyl chloride by a procedure similar to that described by Villieras and Rambaud (10). The chloride boiled at 68-70 °C (19 mm) and was obtained in 38% yield. ^{1}H NMR spectrum: ($CDCl_3$) δ 4.13 (2H, s), 6.07 (2H, s).

Ethyl α-(Bromomethyl)acrylate (**VII**)

This was prepared by the method of Villieras and Rambaud (10).

α-(Bromomethyl)styrene (**VIII**)

This compound was obtained by the method of Pines and coworkers (11).

α-(Diethoxyphosphorylmethyl)styrene (**IX**)

α-(Bromomethyl)styrene was treated with an equimolar ratio of triethylphosphite at reflux for 1 h. After the ethyl bromide was removed *in vacuo*, the residue was purified by chromatography on silica gel (ethyl acetate/petrol 3:2) to give **IX** (54%). ^{1}H NMR spectrum: ($CDCl_3$) δ 1.20 (6H, t, J = 7.5 Hz), 3.05 (2H, d, J = 22.5 Hz), 4.00 (4H, m), 5.35 (1H, d, J = 6 Hz), 5.50 (1H, d, J = 6 Hz), 7.25-7.55 (5H, m).

α-(*n*-Butanethiomethyl)styrene (**XI**)

A mixture of α-(bromomethyl)styrene (3.5 g), *n*-butanethiol (1.8 g), potassium carbonate (2.7 g) and methanol (25 ml) were stirred for 15 h at room temperature. After this time the mixture was poured into water and extracted with ether. After drying of the extract and removal of the solvent, the residue was chromatographed on silica gel (petroleum spirit) to afford the thioether (3.3 g, 90 %). ^{1}H NMR spectrum: ($CDCl_3$) δ 0.85 (3H, t, J = 7 Hz), 1.20-1.70 (4H, m), 2.45 (2H, t, J = 7 Hz), 3.58 (2H, s), 5.20 (1H, s), 5.40 (1H, s), 7.20-7.50 (5H, m).

α-(*n*-Butanesulfinylmethyl)styrene (**X**)

m-Chloroperbenzoic acid (0.93 g) in dichloromethane (25 ml) was added to a stirred solution of α-(*n*-butanethiomethyl)styrene (1 g) in dichloromethane (25 ml) at -78 °C. The mixture was allowed to stir for 1 h at -78 °C, before being poured into saturated sodium

bicarbonate solution (50 ml). The organic layer was separated and the aqueous phase was extracted three times with dichloromethane. The combined organic phases were then washed with water, dried over anhydrous sodium sulfate, and the solvent was removed to give α-(*n*-butanesulfinylmethyl)styrene (1.05 g, 97%), mp 42-43.5 °C (from petroleum spirit). ^{1}H NMR spectrum: ($CDCl_3$) δ 0.90 (3H, t, J = 7 Hz), 1.20-1.90 (4H, m), 2.65 (2H, t, J = 7 Hz), 3.80 and 3.95 (2H, ABq, J_{AB} = 15 Hz), 5.35 (1H, s), 5.55 (1H, s), 7.20-7.50 (5H, m). IR spectrum: (film) ν_{max} 1040 cm^{-1}. MS: (CH_4) *m/z* 223 (MH^+, 100 %), 117 (15 %).

Ethyl α-(Tri-*n*-butylstannylmethyl)acrylate (**XII**)

This compound was prepared by the procedure described by Baldwin and coworkers (8).

Ethyl α-(Trimethylsilylmethyl)acrylate (**XIII**)

The method described by Haider (12) was used to prepare this silyl compound.

Ethyl α-(Benzenesulfonylmethyl)acrylate (**XIV**)

This compound was prepared as described by Baldwin and coworkers (8).

α-(Benzenesulphonylmethyl)vinyl Acetate (**XV**)

This compound was prepared from propynyl phenyl sulfone in an analogous manner to that decribed by Appleyard and Stirling (13) for the preparation of α-(toluenesulphonylmethyl)vinyl acetate. ^{1}H NMR spectrum: ($CDCl_3$) δ 1.97 (3H, s), 4.03 (2H, s), 4.83 (1H, d, J = 2.3 Hz), 5.03 (1H, d, J = 2.3 Hz), 7.4-8.2 (5H, m). IR spectrum: (film) ν_{max} 1665, 1770 cm^{-1}. MS: (CH_4) *m/z* 241 (MH^+, 29 %), 199 (100 %).

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