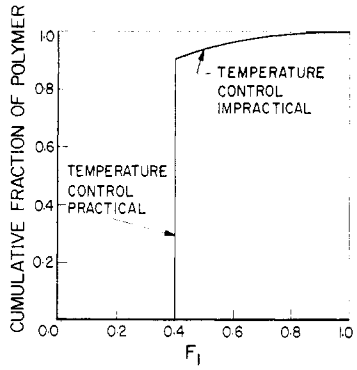

Figure 5. The copolymer composition distribution when complete compensation is impractical.

be treated, by picking the initial monomer concentrations so that the greatest volume of polymer is produced in the region where temperature compensation is possible. Figure 5 illustrates the shape of the CCD in this case when a monodisperse polymer is desired.

Although the temperature variations proposed will tend to widen the molecular weight distribution (MWD), it is felt that this temperature control scheme has great practical advantage for control of copolymerization reactors when MWD effects are not critical and the required heat transfer is allowed for at the design stage.

Appendix

Let us determine the conditions under which eq 13 has positive real solutions. Let

$$g(r_2) = r_2^n - ar_2 - b \qquad (16)$$

Since

$$g'(r_2) = nr_2^{n-1} - a \qquad (17)$$

$$g''(r_2) = n(n - 1)r_2^{n-2} \qquad (18)$$

we can now determine the character of $g(r_2)$.

i. $n < 0$**.** In this case $g(0) \rightarrow \infty$, $g(r_2 \rightarrow \infty) \rightarrow -\infty$, $g''(r_2) > 0$ (*i.e.*, g is strictly convex) so that there is one and only one root to eq 16 when $n < 0$.

ii. $0 \leq n < 1$**.** In this case $g(0) = -b$

$$\lim_{r_2 \rightarrow \infty} g(r_2) \rightarrow -\infty$$

and g is strictly concave so that if $b < 0$, then there is one only one root to eq 16 and when $b \geq 0$ there is either zero or two roots to eq 16 depending on the value of $g(r_2)$ when it attains its maximum. The maximum value of $g(r_2)$ (gotten by setting eq 17 to zero) is given by

$$g_{\mathrm{m}} = a^{n/n-1}\left[\frac{1 - n}{(n)^{n/n-1}}\right] - b \qquad (19)$$

and thus $g_{\mathrm{m}} \geq 0$ is required for 16 to have a solution.

iii. $n > 1$**.** In this case $g(0) = -b$

$$\lim_{r_2 \rightarrow \infty} g(r_2) \rightarrow +\infty$$

and g is strictly convex so that if $b > 0$ there is one and only one solution to eq 16. For $b \leq 0$ we must require the minimum value of g, eq 19, to be nonpositive for eq 16 to have a solution.

Acknowledgment. The authors are indebted to Mr. Amar Mohan for performing the calculations and to the Department of University Affairs of Ontario for research support.

Telomerization by Free Radical Mercaptan Chain Transfer. III. Chain Transfer Constants and Stereospecificity in the Methyl Acrylate–Ethanethiol System[1]

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ABSTRACT: Previous determinations of methyl acrylate–ethanethiol chain transfer constants have been refined and extended to five-unit radicals. Values higher than C_1 are nearly constant and essentially equal to the average for long chains; therefore no reactivity minimum exists, and telomer addition steps are suitable kinetic models for polymerization. Three-unit diastereomers have been separated and quantitatively measured. The isotactic and syndiotactic mole fractions were found to be nearly equal and constant over wide ranges of monomer–mercaptan ratio and temperature, showing that the two modes of addition differ little in entropy and enthalpy of activation.

Studies of free-radical telomerization are useful in elucidating details of corresponding polymerizations. However the inherent advantage offered by direct observation of pure monodisperse fractions may be offset by complicating end-group effects unless these are thoroughly understood. This paper is concerned with application of the telomer approach to investigation of free-radical additions of methyl acrylate; at the outset it was thought that a serious complicating end-group effect might exist.

In 1964, rough measurements of the chain transfer constants for the first three methyl acrylate–ethanethiol

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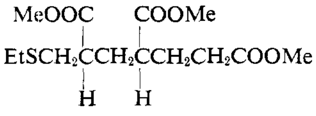
(1) Reported in part at the Midwest Regional Meeting of the American Chemical Society, Manhattan, Kansas, Nov 1968.

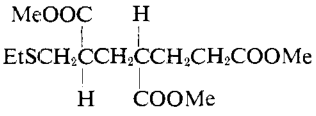
telomerization steps were reported from this laboratory.[2] The probable range of these values for the three-unit telomer radical (C_3), though quite broad (2.0–19.0), suggested that a limited reactivity minimum might occur in this system. This was considered possible since it seemed to parallel much more dramatic effects observed by British workers[3] in several bromotrichloromethane systems. This possibility was of special interest partly because of the semibond theory proposed by Kirkham and Robb[3b] to explain their results, although explanations based on intramolecular chain transfer seemed more probable. In either case more work was needed to decide whether the phenomenon did actually appear in the thiol system.

This report describes a thorough and precise reinvestigation of chain transfer constants for radicals up to five units in length. Since the results apparently dispose of the reactivity minimum question for this system, further work promises information applicable to polymerization. Accordingly a study of stereospecificity in telomer formation using gas chromatography and nmr has been undertaken starting with the simplest possible step, namely, formation of the three-unit diastereomers, I and II. Initial quantitative experiments have been made on these over wide ranges of monomer–thiol ratio



$$\mathrm{EtSCH_2\underset{H}{\overset{MeOOC}{C}}CH_2\underset{H}{\overset{COOMe}{C}}CH_2CH_2COOMe}$$

I Isotactic



$$\mathrm{EtSCH_2\underset{H}{\overset{MeOOC}{C}}CH_2\underset{COOMe}{\overset{H}{C}}CH_2CH_2COOMe}$$

II Syndiotactic

and temperature; results and implications of this work are also reported and discussed below.

Experimental Section

Telomer Preparations and Separations. In general telomers were prepared and characterized using materials and procedures already described.[2] The first three telomers were separated and purified by vacuum distillation. It was found that higher telomers (up to at least seven units) could be separated into fractions monodisperse with respect to degree of polymerization by column chromatography using Mallinckrodt 100 mesh silicic acid (analytical grade, 80 g/g of sample) as adsorbant. Mixtures of petroleum ether and increasing amounts of ethyl ether were used as eluting solvents at flow rates of about 2 ml/min. Identity and purity of resulting fractions were monitored by thin layer chromatography on silica gel H using petroleum ether, ethyl ether, acetic acid mixtures (50:50:1) as solvent and iodine vapors to develop the spots. It was also possible to observe telomers up to seven units by gas chromatography using a 1.5 ft × 0.25 in. column containing 10% SE-52 (phenyl silicone) on Gas Chrom Z in an F & M Model 700 gas chromatograph with a flame ionization detector. Column temperatures in the range 60–285° were used. In the case of higher telomers injections were made in the form of roughly 3% acetone solutions. Wide separations and well-shaped Gaussian-form curves resulted.

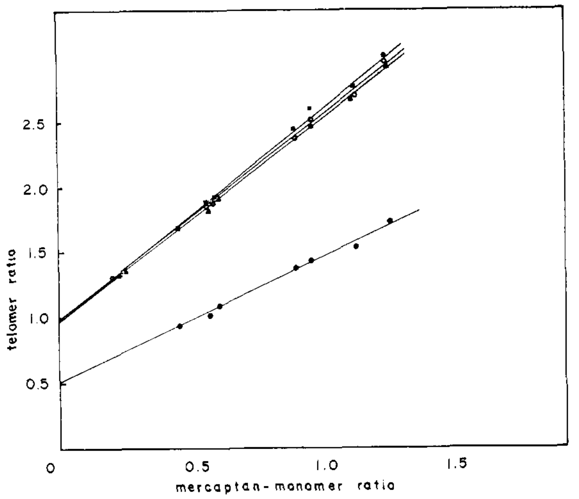


Figure 1. Mole ratios of telomers $n/(n + 1)$ units as a function of mercaptan/monomer mole ratio at low conversion at 50°; ●, $n = 1$; ■, $n = 2$; ○, $n = 3$; ▲, $n = 4$.

Using columns 0.25 in. × 4 ft coated with 5% butanediol succinate on Gas Chrom Z in the same instrument, partial separation of the diastereomers of the three-unit telomer was observable. Small samples of each diastereomer were subsequently separated in relatively pure states using an 8 ft × 0.25 in. column containing 10% butanediol succinate on Gas Chrom Z in an Aerograph Autoprep A-700 and also by column chromatography as described above using 20% ethyl ether in petroleum ether (bp 30–60°) as eluting solvent.

Quantitative Measurements. Telomer ratios were determined quantitatively in reaction mixtures resulting from thiol and monomer in mole ratios between 0.2 and 2.6 sealed in acid-washed Pyrex tubes under nitrogen and allowed to react at 50°. In the absence of added initiator, it was found that this procedure resulted in consumption of 1–3% of monomer in 1–2 hr. Presumably adventitious peroxide formed after distillation (*cf.* ref 4) was the source of initiation. (No reaction occurred in the presence of hydroquinone inhibitor.) Chromatograms were obtained directly from untreated mixtures or, in the case of high telomers, from mixtures concentrated by bubbling nitrogen through at 0° for about 10 min. Mole ratios were calculated from area ratios measured by a Disc Chart integrator, Model 204, on the basis of calibration using pure telomers as standards. Nmr spectra were run on a Varian A60 A spectrometer. Infrared spectra were obtained with a Perkin-Elmer 237B spectrometer.

Stereospecificity Experiments. Telomerizations for study of three-unit diastereomer ratios were carried out in the presence of 0.2 mol % of azobisisobutyronitrile. At 35° and above they were carried out thermally in sealed tubes as previously described. At 0 and −30° a 25-W Pen-Ray uv lamp was used to provide photochemical initiation in a flask filled with nitrogen at atmospheric pressure cooled in an ice bath and a Dry Ice–acetone bath, respectively. At −80° the reaction was found to be too slow for practical measurement.

Results and Discussion

Area ratios obtained as described above are plotted as a function of mercaptan-to-monomer mole ratio in

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(2) G. P. Scott, C. C. Soong, W. S. Huang, and J. L. Reynolds, *J. Org. Chem.*, **29**, 83 (1964).

(3) (a) J. C. Robb and E. Senogles, *Trans. Faraday Soc.*, **58**, 708 (1962); (b) W. J. Kirkham and J. C. Robb, *ibid.*, **57**, 1757 (1961); (c) J. C. Robb and D. Vofsi, *ibid.*, **55**, 558 (1959); (d) W. I. Bengough and R. A. M. Thompson, *ibid.*, **57**, 1928 (1961); (e) *ibid.*, **56**, 407 (1960).

(4) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, New York, N. Y., 1954, p 23.

Table I
Chain Transfer Constant Data on Methyl Acrylate–Ethanethiol Telomerization at 50°

Constant	Value from slope[a]	Estimated error[b]	Value from slope/intercept[a]	Estimated error[b]
C_1	0.94	±0.07		
C_2	1.65	±0.12	1.84	±0.40
C_3	1.57	±0.09	1.73	±0.33
C_4	1.52	±0.06	1.65	±0.16
C_5			1.55	±0.16
C_∞[c]	1.57	±0.18		

[a] Values are based on least squares calculation assuming linearity. [b] 5% probability level. [c] Value from ref 2.

Figure 1. Fom these data calculated telomer ratios corresponding to each series of area ratios were substituted in the left side of the equation

$$\frac{\mathrm{d}[\mathrm{B} - \mathrm{M}_n - \mathrm{A}]}{\mathrm{d}[\mathrm{B} - \mathrm{M}_{n+1} - \mathrm{A}]} = C_n[\mathrm{AB}]/[\mathrm{M}] + C_n/C_{n+1}$$

where [M] and [AB] are the monomer and thiol concentrations, respectively, and C_n and C_{n+1} refer to chain transfer constants of the radicals of the specified length (*cf.* ref 2). Chain transfer constants based on linear least squares calculations (slopes and slopes/intercepts) are listed together with corresponding ranges of probable errors in Table I. It will be noted that values of constants obtained from slopes and intercepts check each other within probable experimental limits. It is further noted that, except for C_1, chain transfer constants do not vary appreciably with increasing chain length and do not differ substantially from the average value for long chains (C_∞). These results were obtained with better instrumentation and involved more direct measurement and milder treatment than those previously reported,[2] and showed very good reproducibility. There is, therefore, no evidence for a reactivity minimum in this system; moreover, it appears that the thioethyl end group does not appreciably affect the reactivity of a growing methyl acrylate radical chain beyond the first unit. Since end-group effects are negligible, one-step-at-a-time kinetic studies, etc., are of interest for direct comparison with long-chain methyl acrylate polymerization. In consequence of these results a study of ratios of three-unit diastereomers appeared promising as an attack on the problem of stereospecificity in free-radical methyl acrylate addition.

Detailed nmr studies of stereoregularity in long chain polymers have recently been summarized by Bovey.[5] Of the limited number of polymers studied, most complete information is available on poly(methyl methacrylate), since its methylene and α methyl band systems are uncomplicated by vicinal coupling and reflect tacticity sequences in relatively simple ways. It has been shown that syndiotactic coupling is favored in the free radical case and that, owing to the difference in activation energies between orientations, a substantially greater syndiotactic preference exists at low temperatures. It has further been shown that penultimate effects are absent, tacticity being influenced only by the last monomer unit in the radical chain. Thus it can be quantitatively expressed by a single Bernoullian statistical parameter, here designated P_m, which represents the fraction of units adding isotactically. In poly(methyl methacrylate) this has been reported to vary from 0.13 to 0.27 over the temperature range −78 to 100°.

Poly(methyl acrylate), owing to spin–spin coupling between methylene and α-methine protons, has a more complex nmr spectrum and no corresponding information has been reported, although band assignments have been made and stereoregularity of a poly(methyl acrylate) derived from hydrolyzed polyacrylonitrile-α-*d* has been estimated.[6] In free-radical poly(vinyl chloride), another polymer possessing α hydrogens, values of P_m have been reported to vary only from 0.43 to 0.46 in the temperature range 0–100° (0.37 at −78°) showing greater similarity of enthalpy and entropy of activation between the two addition orientations than in the more sterically hindered methyl methacrylate case.[5]

In a corresponding telomer nmr spectra are complicated not only by mutual vicinal coupling, but also by lack of effective end-to-end chain symmetry and by variation of proton positions with respect to end structures. However glpc separations such as those observed in this system afford a basis for quantitative investigations. Addition stereospecificity can be related to three-unit telomer ratios by consideration of eq 1–6

$$\mathrm{B{-}M_2\cdot} + \mathrm{M} \xrightarrow{k_s} \mathrm{B{-}M_{3s}\cdot} \tag{1}$$

$$\mathrm{B{-}M_2\cdot} + \mathrm{M} \xrightarrow{k_i} \mathrm{B{-}M_{3i}\cdot} \tag{2}$$

$$\mathrm{B{-}M_{3s}\cdot} + \mathrm{B{-}A} \xrightarrow{k_a} \mathrm{B{-}M_{3s}{-}A} + \mathrm{B\cdot} \tag{3}$$

$$\mathrm{B{-}M_{3s}\cdot} + \mathrm{M} \xrightarrow{k_b} \mathrm{B{-}M_4\cdot} \tag{4}$$

$$\mathrm{B{-}M_{3i}\cdot} + \mathrm{B{-}A} \xrightarrow{k_c} \mathrm{B{-}M_{3i}{-}A} + \mathrm{B\cdot} \tag{5}$$

$$\mathrm{B{-}M_{3i}\cdot} + \mathrm{M} \xrightarrow{k_d} \mathrm{B{-}M_4\cdot} \tag{6}$$

where M's represent monomer units, number and orientations being designated by appropriate subscripts (2, 3, i, s for two-unit, three-unit, isotactic, and syndiotactic), and A and B represent fragments of the chain transfer agent (H and EtS, respectively). Applying the usual steady-state approximation it is readily shown that the three-unit diastereomer ratio at low conversion is given by the equation

$$\frac{\mathrm{d}[\mathrm{B{-}M_{3i}{-}A}]}{\mathrm{d}[\mathrm{B{-}M_{3s}{-}A}]} = \frac{k_i k_c}{k_s k_a}\frac{([\mathrm{B{-}A}]k_a + [\mathrm{M}]k_b)}{([\mathrm{B{-}A}]k_c + [\mathrm{M}]k_d)}$$

In the absence of penultimate effects it is to be expected that $k_a = k_c$ and $k_b = k_d$. On this basis $[\mathrm{B{-}M_{3i}{-}A}]/\mathrm{d}[\mathrm{B{-}M_{3s}{-}A}]$ becomes simply k_i/k_s or $P_m/(1 - P_m)$, and the diastereomer ratio is independent of the ratio of monomer to chain transfer agent.

Figure 2 displays a typical gas chromatogram of the three-unit diastereomers showing partial separation. Chromatograms of samples separated with the Autoprep are shown in Figure 3. It will be noted that cross-contamination is slight as indicated by the small size of shoulders. Infrared spectra of these samples were

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[5] F. A. Bovey, *Accounts Chem. Res.*, **1**, 175 (1968).

[6] K. Matsuzaki, T. Uryu, and A. Ishida, *J. Polym. Sci., Part C*, **16**, 2099 (1967).

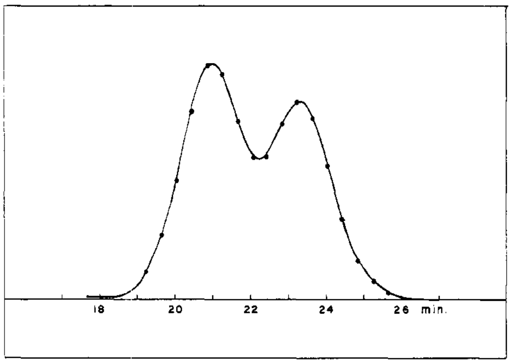

Figure 2. Gas chromatogram showing partial separation of three-unit telomer diastereomers.

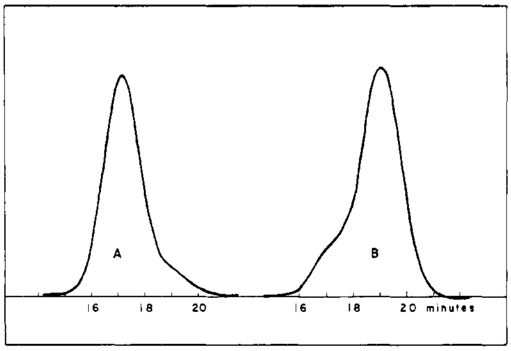

Figure 3. Gas chromatograms of separated three-unit telomer diastereomers.

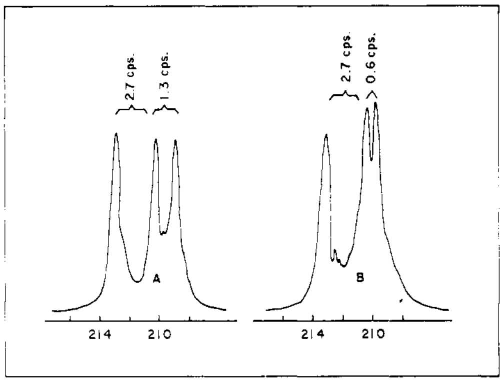

Figure 4. Nmr spectra of three-unit telomer diastereomers in the ester methoxyl proton region. Frequency is in cycles per second below TMS at 60 mc.

found to be identical except for a small shoulder at 1025 cm^{-1} present in the spectrum of the second isomer to elute, but more significant differences appear in the nmr spectra. These are obvious in Figure 4, which shows the two sets of ester methoxyl bands at high resolution; however, owing to the complexity already mentioned, it has not yet been possible to prove from these spectra which isomer is which.

Quantitative estimation from glpc data of relative amounts was carried out by least-squares digital computer simulation using a Fortran II program based on summation of two overlapping Gaussian functions of the form

$$y = a \exp\{-(x - b)^2/c\} + r \exp\{-(x - s)^2/t\}$$

Observed and mathematically simulated curves agreed in all cases within experimental error. Typical calculated points are shown on the experimental chromatogram in Figure 2. Relative amounts of isomers were assumed proportional to calculated areas under the corresponding Gaussian components. In each case the peak for the second component, although somewhat lower, was found a little broader and only slightly less in area. Fractions of the two isomers determined on this basis are listed in Table II.

Conclusions

In Table II it will be noted that diastereomer mole fractions are approximately equal and also generally invariant. Specifically the constancy shown in runs 2, 3, and 4, in which the mercaptan-to-monomer ratio varies widely, are consistent with the expected absence of penultimate effect. If methyl acrylate like methyl methacrylate favors syndiotactic addition, it follows that B is the isotactic form and mole fractions in the last column are equal to P_m. The constancy of these values with temperature leads to the general conclusion that the difference in enthalpy of activation for the two addition orientations is negligible, and the approximate 1:1 ratio of values in the last two columns shows that the corresponding difference in entropy of activation is small. This implies that free-radical poly(methyl acrylate) is probably among the most atactic of common polymers. This is not too surprising since stereospecificity observed in poly(methyl methacrylate) has been explained largely on the basis of nonbonded interactions, which should be much less in this system. These results appear consistent with the very limited data available on the general problem of free-radical polymer tacticity.[7]

TABLE II
THREE-UNIT TELOMER DIASTEREOMER MOLE FRACTIONS

Run no.	Reaction conditions Mercaptan-monomer mole ratio	Temp, °C	Product mole fractions[a] A	B
1	0.81	95	0.533	0.467
2	4.5	50	0.536	0.464
3	0.81	50	0.536	0.464
4	0.30	50	0.534	0.466
5	0.81	0	0.536	0.464
6	0.81	−30	0.532	0.468

[a] Diastereomers are designated A and B in order of the elution as shown on the chromatogram.

A thorough study is now being made of nmr spectra of this whole series of telomers, and should eventually clear up any doubt as to the identity of the diastereomers. The chain transfer data described above appears to establish the suitability of mercaptan telomer investigations as an approach to the acquisition of microstructure and kinetic information applicable to free radical polymers. This approach would seem to be limited primarily by the problem of separating diastereomers. Cases such as this should serve as valuable bases for study of the influence of possible effects of solvents, complexing agents, surface or interlayer adsorption, etc., on stereospecificity. Such studies are now being attempted in this laboratory.

(7) D. A. Smith, "Addition Polymers, Formation and Characterization," Plenum Press, New York, N. Y., 1968, p 314.