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Quasiliving Carbocationic Polymerization. XVI. Forced Ideal Terpolymerization of Styrene- α -Methylstyrene-Isobutylene

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ABSTRACT

Forced ideal carbocationic terpolymerization of styrene/ α -methylstyrene/isobutylene systems has been achieved by continuous addition of mixed monomer feeds to 2-chloro-2,4,4-trimethylpentane/ TiCl_4 initiator/coinitiator charges dissolved in n-hexane/methylene chloride solvent mixtures. The compositions of terpolymers were uniform and identical to those of the feeds in the concentration ranges studied. The number-average molecular weights increased monotonously with the amounts of monomers consumed; however,

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pronounced chain transfer to monomer was evident. The microstructure of the products was investigated by ^{13}C -NMR spectroscopy. According to dual detector GPC, ^{13}C -NMR and DSC data true terpolymers have formed.

INTRODUCTION

In quasiliving homopolymerization, initiation is virtually instantaneous, termination is absent or reversible, and chain transfer to monomer is much depressed [1]. Quasiliving conditions may be achieved by the continuous addition of a monomer feed to an initiating system charge provided that the rate of monomer addition is equal to that of monomer consumption (polymerization) [2]. In quasiliving systems the molecular weights increase linearly with the amount of monomer introduced so that molecular weight control is feasible with relatively narrow molecular weight distributions [2].

The copolymerization of various monomer pairs under quasiliving conditions has also been demonstrated [3, 4]. In quasiliving copolymerizations a comonomer feed is introduced to an active charge at the same rate the two monomers are consumed. In this manner the overall composition of the monomer feed and the copolymer product must remain the same and the system for all practical purposes behaves as an ideal copolymerization over the entire compositional range. We coined the term "forced" ideal quasiliving copolymerization to describe such systems [3].

Having demonstrated the feasibility of forced ideal copolymerization of two monomers [3, 4], we explored the possibility of terpolymerizing three monomers under quasiliving conditions. Carbocationic terpolymerizations is a practically uncharted territory: Even the cationic copolymerization of monomer pairs is a difficult undertaking because of the usually large monomer reactivity differences, let alone terpolymerizations. It occurred to us that by the use of the quasiliving polymerization principle we could "force" terpolymerizations to occur and in this manner hosts of interesting new products could be created.

This paper concerns the forced ideal quasiliving terpolymerization of St- α MeSt-iBu systems and a demonstration that the composition of the mixed monomer feed and that of the terpolymer product are identical.

EXPERIMENTAL

Materials

Styrene, α -methylstyrene, and isobutylene were purified by standard methods described earlier [2, 3, 5]. n-Hexane was treated with oleum to remove olefinic impurities, then washed neutral with distilled water,

dried over molecular sieves (3 Å), and distilled from CaH_2 under nitrogen. Methylene chloride was purified as described [6]. 2-Chloro-2,4,4-trimethylpentane was synthesized by hydrochlorination of 2,4,4-trimethyl-1-pentene (Aldrich). TiCl_4 was distilled from P_2O_5 under nitrogen atmosphere.

Procedures

Polymerizations were carried out in a stainless-steel enclosure under dry N_2 at -50°C in 250 cm^3 three-neck round-bottom flasks equipped with stirrer, Teflon plug for monomer addition, and outlet for sampling. The initial volume of the charge was 100 cm^3 (60 cm^3 n-hexane + 40 cm^3 methylene chloride). 2-Chloro-2,4,4-trimethylpentane initiator (1×10^{-3} mol) and TiCl_4 coinitiator (2×10^{-3} mol) were added to the solvent mixture. After 5 min premixing, the introduction of St/ α MeSt/iBu/ CH_2Cl_2 mixture started. The monomer feed was injected into the well-stirred charge by forcing it through a precision bore glass capillary by nitrogen pressure.

During the polymerization small aliquots (0.1 cm^3) were withdrawn with a syringe from the reaction mixture and were injected into capped vials containing excess methanol. Polymerizations were stopped by adding methanol. Conversions were determined gravimetrically.

Molecular weights were determined by a Waters Associates High Pressure GPC equipped with five Microstyrigel columns (10^5 , 10^4 , 10^3 , 5×10^2 , and 10^2 Å) and dual UV/RI detectors. Molecular weights were calculated by the use of a calibration curve obtained with polystyrene standards.

Terpolymer compositions were determined by integration of ^1H -NMR resonances using a Varian T-60 NMR Spectrometer and CDCl_3 solutions at room temperature. ^{13}C -NMR spectra were recorded on a Varian FT-20A instrument using CDCl_3 solutions at room temperature. T_g 's were determined by DuPont Instruments 1090 Thermal Analyzer at a heating rate of $5^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

It has been demonstrated that copolymers whose composition is uniform and identical to the feed can be obtained by ideal quasilinging copolymerization [3]. In a conventional living batch copolymerization the composition of the charge is continuously shifting with conversion and consequently the sequence composition of the copolymer product must also shift along as dictated by the reactivity ratios. In contrast, under quasilinging conditions the composition of the feed remains always

constant, and the monomers are instantaneously and completely consumed; thus the overall copolymer composition will be identical to that of the feed. One may view a forced ideal copolymerization as a series of living microbatch copolymerizations.

The equations that describe the composition of a copolymer obtained by forced ideal quasilinging copolymerization have been presented [3]. It has been shown that

$$[M_1^P]/[M_2^P] = A_1/A_2 \quad (1)$$

where $[M_1^P]$ and $[M_2^P]$ are the concentrations of monomer units M_1 and M_2 in the polymer, respectively, and A_1 and A_2 are the input rates of M_1 and M_2 to a copolymerization charge. Thus copolymer composition is solely determined by the monomer feeding rate and is independent of the reactivity ratios. While the average or overall copolymer composition is independent of r_1 and r_2 , the microsequence distribution is still determined by these parameters.

The terpolymer composition obtained in a quasilinging system can be derived by extending the treatment developed for copolymer systems [3]. Thus the feeding of a mixture of three monomers (M_1 , M_2 , and M_3) to an active terpolymerization charge with an input rate of

$$A = A_1 + A_2 + A_3 \quad (2)$$

yields the following respective monomer concentrations in the charge (neglecting monomer consumption by chain transfer):

$$d[M_1]/dt = A_1 - (k_{11}\alpha_1 + k_{21}\alpha_2 + k_{31}\alpha_3)[I]_0[M_1] \quad (3a)$$

$$d[M_2]/dt = A_2 - (k_{12}\alpha_1 + k_{22}\alpha_2 + k_{32}\alpha_3)[I]_0[M_2] \quad (3b)$$

$$d[M_3]/dt = A_3 - (k_{13}\alpha_1 + k_{23}\alpha_2 + k_{33}\alpha_3)[I]_0[M_3] \quad (3c)$$

where the A 's stand for the monomer input rates, $\alpha_1 = [M_1^\oplus]/([M_1^\oplus] + [M_2^\oplus] + [M_3^\oplus])$, i.e., the fraction of propagating cations with M_1 as terminal monomer unit, and similarly

$$\alpha_2 = [M_2^\oplus]/([M_1^\oplus] + [M_2^\oplus] + [M_3^\oplus])$$

and

$$\alpha_3 = [M_3^\oplus] / ([M_1^\oplus] + [M_2^\oplus] + [M_3^\oplus])$$

$[I]_0$ = the number of active centers; the rate constants have the usual meaning.

Under stationary conditions with continuous 100% monomer consumption:

$$d[M_1]/dt \cong 0 \quad d[M_2]/dt \cong 0 \quad d[M_3]/dt \cong 0 \quad (4)$$

and

$$[M_1] = [M_1]_{st} \quad [M_2] = [M_2]_{st} \quad [M_3] = [M_3]_{st} \quad (5)$$

where the subscript "st" refers to the steady state. Thus the individual rates of monomer incorporations into the terpolymer are:

$$d[M_1^P]/dt = (k_{11}\alpha_1 + k_{21}\alpha_2 + k_{31}\alpha_3)[I]_0[M_1]_{st} = A_1 \quad (6a)$$

$$d[M_2^P]/dt = (k_{12}\alpha_1 + k_{22}\alpha_2 + k_{32}\alpha_3)[I]_0[M_2]_{st} = A_2 \quad (6b)$$

$$d[M_3^P]/dt = (k_{13}\alpha_1 + k_{23}\alpha_2 + k_{33}\alpha_3)[I]_0[M_3]_{st} = A_3 \quad (6c)$$

where $[M_1^P]$, $[M_2^P]$, and $[M_3^P]$ are the respective monomer units in the terpolymer. Since the input rates are constant, integration of these rate equations yields

$$[M_1^P] = A_1 t \quad [M_2^P] = A_2 t \quad [M_3^P] = A_3 t \quad (7)$$

and

$$\frac{[M_1^P]}{[M_2^P]} = \frac{A_1}{A_2} \quad \frac{[M_1^P]}{[M_3^P]} = \frac{A_1}{A_3} \quad \frac{[M_2^P]}{[M_3^P]} = \frac{A_2}{A_3} \quad (8)$$

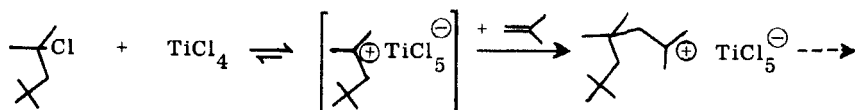
According to these terpolymer composition equations, the composition of the terpolymer is determined only by the monomer addition rates and is independent of the monomer reactivity ratios.

It will be shown that in the St- α MeSt-iBu terpolymer system conversions are 100% throughout the polymerization and that the compositions indeed obey these simple equations (see below).

In contrast to these very simple expressions, the equations describing the composition of terpolymers obtainable in conventional terpolymerizations are more complicated [7, 8].

Forced Ideal Quasiliving Terpolymerization of Styrene- α -Methylstyrene-Isobutylene Mixtures

No systematic studies have been carried out on the terpolymerization of St/ α MeSt/iBu mixtures (or on any kind of cationic terpolymerization system for that matter). First we had to select the most suitable initiating system and solvent medium. Led by past experience we chose TiCl_4 as the coinitiator and felt it necessary to use a $n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ mixture (60/40 v/v) because indanyl-skeleton formation was minimized in this medium [5]. According to Imanishi et al. [9], the reactivity ratio of isobutylene is lower than that of styrene (i.e., 2.6 versus 5.5) in the presence of the " H_2O "/ TiCl_4 system in 75/25 v/v n -hexane/ CH_2Cl_2 mixed solvent system. Thus we anticipated that the least reactive component in our terpolymerization would be the isobutylene and consequently searched for an initiator that would efficiently induce the polymerization of this monomer. Orienting experiments have shown that 2-chloro-2,4,4-trimethylpentane in conjunction with TiCl_4 is an excellent initiator for isobutylene polymerization and for terpolymerization as well:



Subsequently scouting experiments were designed to determine suitable St/ α MeSt/iBu feed compositions to facilitate characterization studies and to find suitable reagent concentration ranges and monomer addition rates. Prior to systematic experimentation, conditions had to be defined under which monomer conversions were demonstrably 100%.

Table 1 summarizes the results of three terpolymerization experiments. In the first experiment (T1--T5) the St/ α MeSt/iBu mole ratio was 2/1/1 (i.e., the mole fraction of iBu was 0.25). The monomers were precooled and mixed, and introduced at a steady rate of 2.4×10^{-2} mol/min by means of a precision pump to a stirred charge of $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2(\text{CH}_3)_2\text{Cl}/\text{TiCl}_4$ in 100 mL $n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ (60/40 v/v) at -50°C . Aliquot samples whose weight, composition, molecular weight, and molecular weight dispersion were determined were withdrawn every 2.5 min. The second and third experiments (T6--T10 and T11--

TABLE 1. Forced Ideal Terpolymerization of Styrene, α -Methylstyrene, and Isobutylene with 2-Chloro-2,4,4-trimethylpentane/TiCl₄ in 60/40 v/v n-Hexane/Methylene Chloride Mixtures at -50°C

Sample	Time (min)	Cumulative amount of added monomers $\times 10^3$ mol	Mole fraction of IB in the terpolymer (¹ H-NMR)	$\bar{M}_n \times 10^{-3}$	$[P] \times 10^{-3}$	\bar{M}_w/\bar{M}_n
Monomer feed molar ratio: ^a 2/1/1; A = 2.4×10^{-2} mol/min; conversion = 100%						
T1	2.5	61		2.8	2.1	3.7
T2	5	122		3.5	3.3	3.3
T3	7.5	183		4.1	4.2	3.4
T4	10	244		4.8	4.8	2.9
T5	12.5	305	0.25	5.1	5.7	2.9
Monomer feed molar ratio: 1/2/1; A = 3.1×10^{-2} mol/min; conversion = 98%						
T6	2	62		2.3	2.7	3.9
T7	4	123		3.0	4.1	3.8
T8	6	185		3.9	4.7	3.3
T9	8	246		4.5	5.5	3.4
T10	10	308	0.25	4.8	6.4	3.0
Monomer feed molar ratio: 1/1/2; A = 5.75×10^{-2} mol/min; conversion = 98%						
T11	2	115		2.4	4.1	5.2
T12	4	230		3.7	5.2	4.8
T13	6	346		4.2	6.9	3.7
T14	8	461	0.50	5.1	7.6	3.3

^a Monomer 1 = styrene; Monomer 2 = α -methylstyrene; Monomer 3 = isobutylene; $I_0 = 1 \times 10^{-2}$ M; TiCl₄ = 2×10^{-2} M.

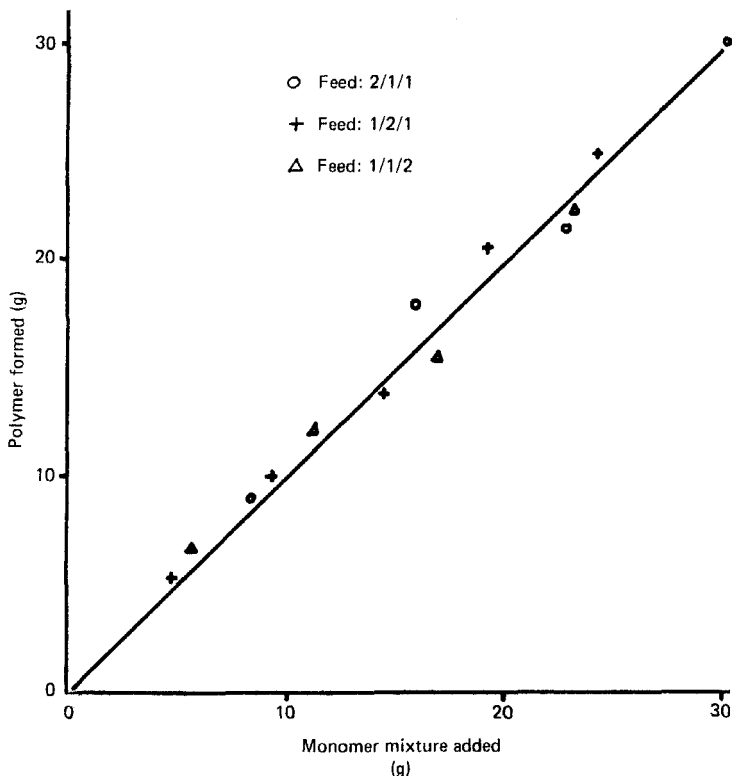


FIG. 1. Amount of polymer formed vs amount of consumed monomer.

T14) were carried out under essentially the same conditions except the composition of the $\text{St}/\sigma\text{MeSt}/i\text{Bu}$ feed was different, i.e., 1/2/1 and 1/1/2, respectively.

Conversions were essentially 100%, thus terpolymer compositions were equal to the composition of the monomer feed. Figure 1 emphasizes these results; it shows that the amount of the polymer formed increases uniformly with the amount of monomer mixture added. Within what is considered to be experimental variation, all the data points can be connected with a master line of 45° slope starting at the origin.

The overall composition of the terpolymers is identical with that of the feeds. This is indicated in the third column of Table 1, i.e., the mol% of $i\text{Bu}$ units in the polymer were 0.25, 0.25, and 0.50 as determined by $^1\text{H-NMR}$ spectroscopy. For comparison, a series of "control" experiments have also been carried out under conventional batch polymerization conditions. In these runs the same initiating system was added to $\text{St}/\sigma\text{MeSt}/i\text{Bu}$ systems of 2/1/1, 1/2/1 and 1/1/2 mol compo-

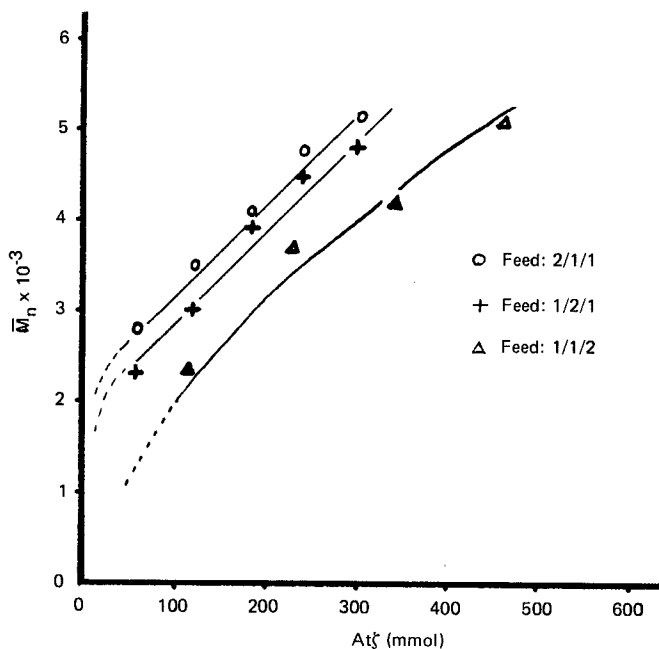


FIG. 2. \bar{M}_n vs cumulative amount of consumed monomer in the terpolymerization of styrene, α -methylstyrene, and isobutylene. ξ = conversion.

sitions of $n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$, 60/40 v/v, -50°C . The overall composition of the products was determined and was found quite different from those of the charges. However, in these experiments the conversions were far from complete.

Figure 2 shows \bar{M}_n versus amount of consumed monomer plots for three different monomer feed compositions. Although the \bar{M}_n increases almost linearly with monomer consumption in every run, the curves cannot be represented by straight lines passing through the origin. Further, Fig. 3 shows the number of polymer molecules P as a function of the amount of monomer added (conversion $\approx 100\%$). According to the plot, P increases steadily during polymerizations due to pronounced chain transfer to monomer. The phenomenon of molecular weight depression in copolymerization is well known [10]. The postulate that the rate of cross-transfer increases more than that of cross-propagation seems to be valid even at slow monomer addition, i.e., at very low monomer concentrations. Because of the reversibility of termination and the presence of transfer, the above system may be classi-

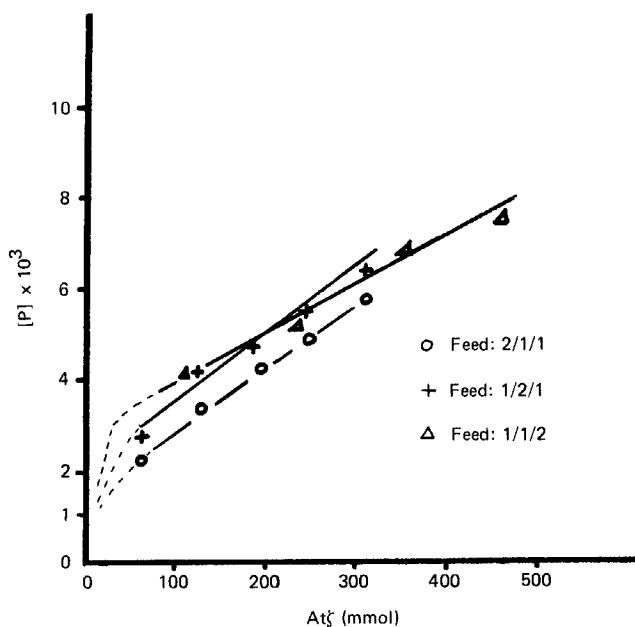


FIG. 3. Number of polymer molecules (P) vs cumulative amount of consumed monomer in the terpolymerization of styrene, α -methylstyrene, and isobutylene. ξ = conversion.

fied as a QL_{RI} system [1]. In these systems the number of polymer molecules increases at a constant rate due to irreversible chain transfer to monomer [1].

Figure 4 demonstrates the importance of using appropriate initiator concentrations and initiator/coinitiator concentration ratios in quasi-living terpolymerization. Three terpolymers of monomer molar ratios $St/\alpha MeSt/iBu = 2/1/1$ were prepared at different initiator concentrations, keeping the other parameters unchanged (see legend to Fig. 4). At a relatively low initiator concentration ($[I_0] = 2.4 \times 10^{-3} \text{ M}$) the GPC trace shows bimodality. The peak at high molecular weights is probably due to polymer that arose by initiation with moisture [5]. (The moisture content in the system was $\sim 10^{-3} \text{ M}$.)

At a relatively high initiator concentration ($[I_0] = 5 \times 10^{-2} \text{ M}$) an appreciably broader molecular weight distribution MWD with a somewhat reduced \bar{M}_n was obtained. These observations may be explained by considering the effect of $[I_0]/[TiCl_4]$ ratio on MWD. By increasing

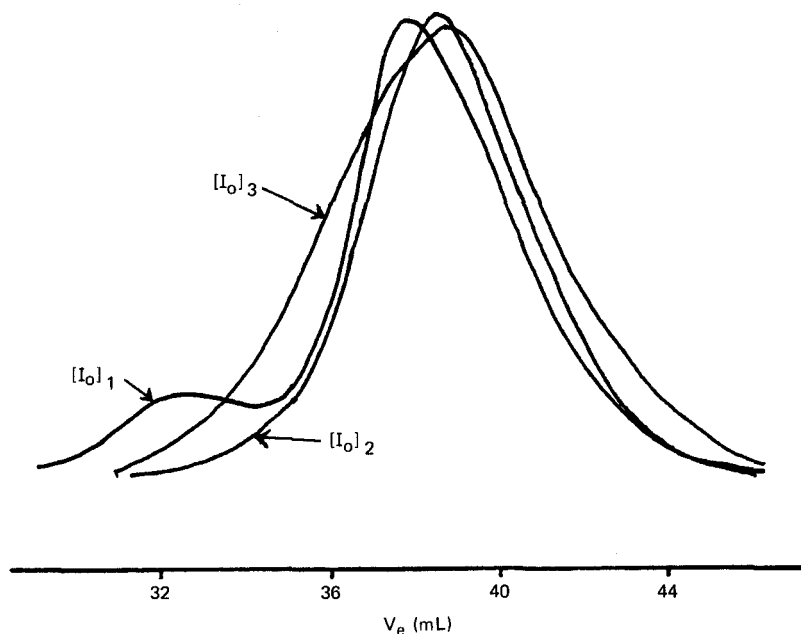
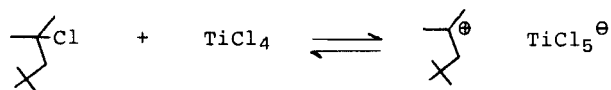


FIG. 4. GPC traces of polymers formed at different $[I_0]/[TiCl_4]$ ratios. $[TiCl_4] = 2 \times 10^{-2}$ M. $[I_0]_1 = 2.4 \times 10^{-3}$ M, $[I_0]_2 = 1 \times 10^{-2}$ M, $[I_0]_3 = 5 \times 10^{-2}$ M.

the $[I_0]$, the $[I_0]/[TiCl_4]$ ratio increases, which leads to a shift toward the right in the ionization equilibrium:



This shift leads to a higher concentration of ionized initiator which in turn results in lower \bar{M}_n . However, due to a higher $[I_0]/[TiCl_4]$ ratio the rate of ionization as well as that of reionization (of the Cl-terminated polymer chain ends) is reduced which leads to a reduced rate of initiation and thus to a broader molecular weight distribution.

Characterization of the Final Products

To prove that the FIQL technique gives rise to truly random terpolymers, the products of the three runs (Samples T5, T10, and T14) have been analyzed by GPC, ^{13}C -NMR, and DSC methods.

Figure 5 shows representative GPC traces. The UV/RI ratios ob-

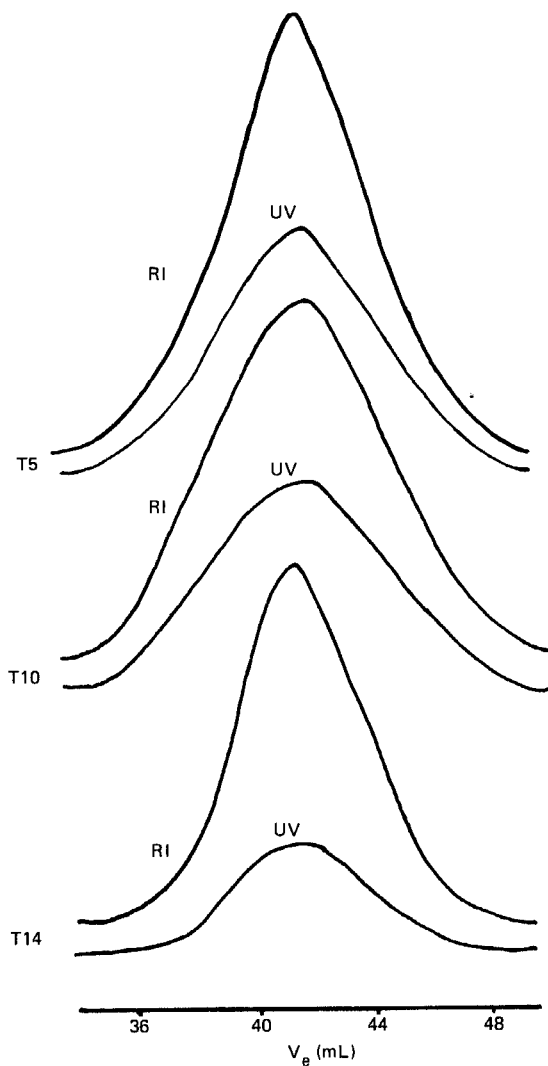


FIG. 5. GPC curves of Samples T5, T10, and T14.

TABLE 2. UV/RI Ratios of the Samples T5, T10, and T14 at Different Elution Volumes

Elution volume (mL)	UV/RI		
	T5	T10	T14
36	0.58	0.57	0.30
38	0.57	0.56	0.29
40	0.58	0.58	0.29
42	0.54	0.58	0.32
44	0.60	0.59	0.31
46	0.57	0.57	0.30
48	0.58	0.55	0.29

tained from this figure are compiled in Table 2. Evidently these ratios are independent of the molecular weights, indicating that the composition of the terpolymer is also independent of the molecular weight.

Figure 6 shows the ^{13}C -NMR spectrum and Table 3 the corresponding peak assignments for Sample T5. Examination of these data indicates a random terpolymer: the resonances at 29.1 and 39.4 ppm are assigned to the $\text{SI}\alpha$ triad which occurs only in a terpolymer. This assignment was derived by knowing the chemical shifts of SII (i.e., 30.2 and 37.1 ppm) and using the formula published by Grant and Paul [11]. The resonances in the 46.0-63.8 ppm region show a complex pattern that is different from the corresponding homo- or copolymers; further the resonances at 47.8, 50.4, 52.7, and 55.2 ppm appear to be novel and are absent in the homo- and copolymers. The exact assignment of methylene carbons of the resonances in this region is rendered extremely difficult by stereoregularity. The other resonances shown in Table 3 are also expected to appear in random $\text{St}/\alpha\text{MeSt}/i\text{Bu}$ terpolymers. The chemical shifts shown have been derived by examining authentic spectra of homo- and copolymers [4, 12].

Figure 7 shows DSC traces of the representative terpolymers (T5, T10, T14) whose overall mole composition is $\text{St}/\alpha\text{MeSt}/i\text{Bu}$ 2/1/1, 1/2/1, and 1/1/2. The traces exhibit only one well-defined T_g for each sample at ~ 72 , 83, and 8°C , respectively. The fact that only one T_g appears in each sample is evidence for the existence of one major homogeneous phase, i.e., random terpolymer. It is of some interest that the experimental T_g 's and those calculated by Fox's

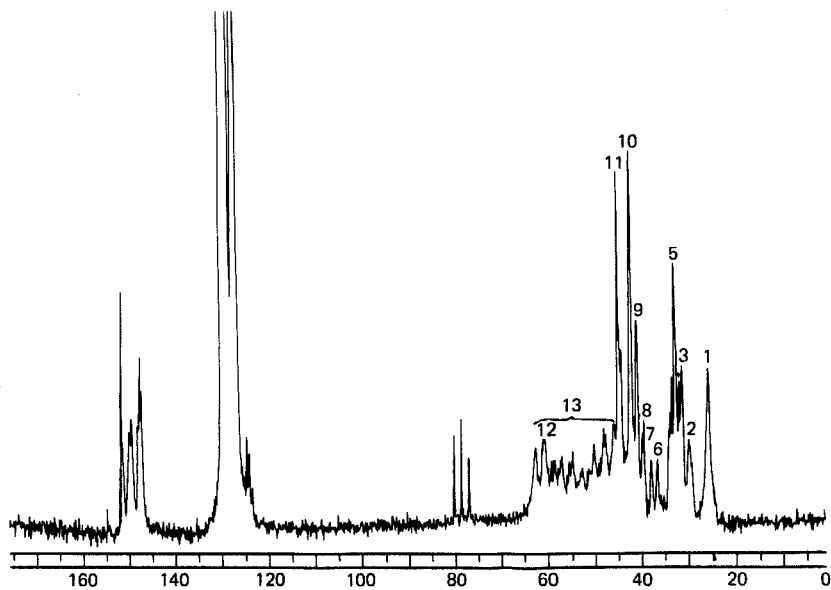


FIG. 6. ^{13}C -NMR spectrum of a St/ σ MeSt/iBu terpolymer (Sample T5).

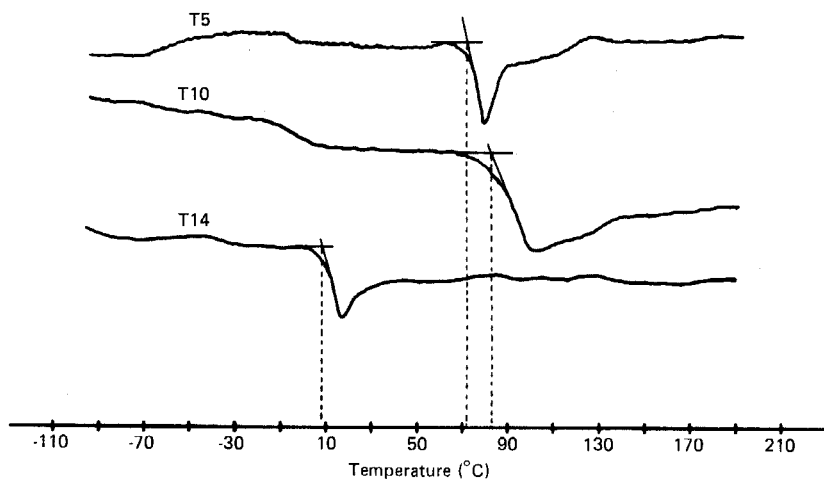


FIG. 7. DSC curves of Samples T5, T10, and T14.

TABLE 3. Chemical Shifts in the ^{13}C -NMR Spectrum of an St/ α -MeSt/IBu Terpolymer

Peak	Chemical shift (ppm)	Identification of the carbon atom		
		St unit (S)	MeSt unit (α)	IBu unit (I)
1	26.0		-CH ₃	
2 a	28.5			-CH ₃ in $\left\{ \begin{array}{l} \text{SIS} \\ \text{SI}\alpha \\ \text{IIS} \end{array} \right\}$ triads
b	29.1			
c	30.2			
3	31.3			-CH ₃ in III triad
4	32.1			-CH ₃ in II α triad
5	32.8			-CH ₃ in α I α triad
6	37.1			-CH ₂ - in IIS and SIS triads
7	38.2			-CH ₂ - in III triad
8	39.4			-CH ₂ - in α I α , α IS, and II α triads
9	41.2	HC- in mixed triads		
10	42.8	HC- in SSS triad (homopolymer)		
11	45.8		-C- in homopolymer	
12	61.0			-C- in homopolymer
13	46.0-63.8	-CH ₂ - in mixed triads		

equation [13] from the overall composition data are not too different: T_g 's of the Samples T5, T10, and T14 are 345 K (calculated: 317 K), 356 K (calculated: 329 K), and 281 K (calculated: 268 K), respectively.

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