

Free radical copolymerization behavior of myrcene

I. Copolymers with styrene, methyl methacrylate or *p*-fluorostyrene

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Summary

Myrcene (7-methyl-3-methylene-1,6-octadiene) binary copolymers with styrene, methyl methacrylate or *p*-fluorostyrene were synthesized. Polymer compositions were measured by ¹H-NMR and reactivity ratios were calculated using a nonlinear least squares error-in-variables method. For myrcene-styrene copolymerizations the polymer radicals have a marked preference for myrcene monomer. In the case of the myrcene-MMA copolymerization the growing polymer chains prefer to add the other monomer, i.e. the crossover reaction dominates. The same is true for the myrcene/*p*-fluorostyrene copolymerization, although the myrcene radical has a higher preference for myrcene monomer in this copolymerization than it does in the myrcene-MMA copolymerization.

Introduction

Myrcene is an isoprene dimer that is found in several naturally occurring materials (1). However, given the structural similarity to isoprene and substituted butadienes, surprisingly little has been done concerning the free radical polymerization or copolymerization of myrcene. There have been studies of myrcene's ionic polymerization behavior (2-9) and studies concerning the incorporation of myrcene into a latex (10), but as far as we could determine by a reasonably thorough search of the literature, no quantitative studies concerning the bulk free radical copolymerization behavior of this monomer have been carried out. Because of an interest in the synthesis of functional polymers and copolymers for various end uses; we decided to investigate the copolymerization behavior of myrcene with common (styrene, MMA) and not so common (*p*-fluorostyrene) monomers. This report details some of our early results.

Experimental

The styrene and methyl methacrylate were commercial grade materials and were purified by distillation from CaH_2 . The myrcene and p-fluorostyrene were obtained from Aldrich² and were purified by distillation from CaH_2 . All monomers were stored in tightly sealed containers at -5°C until used. All other solvents and chemicals used were reagent grade and were used without further purification.

$^1\text{H-NMR}$ spectra were obtained with a Varian Gemini 300 spectrometer operating at 300 MHz (^1H -frequency) in the FT mode. The polymers were dissolved in CDCl_3 and TMS was added as an internal standard. All spectra were recorded at ambient temperature and relative resonance areas were measured by electronic integration. Molecular weight measurements were made with a GPC equipped with a Waters 510 pump, 410 RI detector and two Polymer Labs linear columns (6 x 30 cm). THF was used as an eluent and values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Polymer Synthesis

All the copolymers were synthesized by weighing the desired amounts of the comonomers into clean, dry screw cap vials. The initiator (AIBN, 0.8 wt %) was then added and this mixture was sparged with dry N_2 while cold (-25°C) to minimize loss by evaporation (< 1 wt %). The vials were then placed in a water bath at 65°C for the desired length of time. The vials were removed from the bath, cooled ($\sim 40^\circ\text{C}$) and ~ 5 ml of cold CH_2OH was added. The polymers were purified by reprecipitating them twice from CHCl_3 solution into excess CH_2OH . The polymers were dried in vacuo at ambient temperature for 72h and then weighed to determine conversions.

Results and Discussion

The conversions, molecular weights and copolymer compositions obtained are summarized in Table 1.

The copolymer composition data and feed ratio data obtained were analyzed by using a nonlinear least squares error-in-variables method (11-13). Briefly, the method accounts for the errors in all the measured variables in a copolymerization experiment and treats the resulting error in the calculated reactivity ratios as joint error. In the present cases the error in weighing the monomers into the polymerization vials was estimated as 2% (five place analytical balance). The error in measuring the copolymer composition was estimated at 10% (repeated measurements). The joint confidence intervals that were obtained at the 95% confidence level for the reactivity ratios of the monomer pairs used in this study are shown in Figure 1. The point estimates of the reactivity ratios (+ signs in the Figure) are given in Table 2.

TABLE 1
 Monomer Feed Compositions, Conversions, Molecular Weights and Copolymer Compositions

Polymer	Mole Fraction Myrcene in Feed	Mole Fraction Styrene in Feed	Mole Fraction MMA in Feed	Mole Fraction p-fluoro styrene in Feed	Pzn time (h)	Conv. (wt %)	M_n	M_w	M_f Myrcene in Copolymer
MYRS1	0.83	0.17	-	-	5.0	5.4	3000	5700	0.86
MYRS2	0.71	0.29	-	-	5.0	5.2	7100	11800	0.76
MYRS3	0.64	0.36	-	-	5.0	4.5	-	-	0.70
MYRS4	0.55	0.45	-	-	5.0	7.7	6600	14000	0.61
MYRS5	0.48	0.52	-	-	5.0	7.2	7800	16000	0.55
MYRS6	0.41	0.59	-	-	5.0	8.9	8600	16400	0.46
MYRS7	0.33	0.67	-	-	5.0	9.9	11200	19000	0.38
MYRS8	0.29	0.71	-	-	5.0	9.7	14000	26600	0.33
MYRS9	0.20	0.80	-	-	5.0	11.6	13500	24900	0.23
MYRS10	0.17	0.83	-	-	5.0	16.9	17000	30000	0.18
MYRS11	0.09	0.91	-	-	4.5	13.0	19000	36900	0.10
MYRM1	0.82	-	0.18	-	3.5	1.9	12600	20500	0.73
MYRM2	0.65	-	0.35	-	3.5	3.6	13000	22000	0.62
MYRM3	0.57	-	0.43	-	3.5	3.0	15000	24000	0.59
MYRM4	0.47	-	0.53	-	3.5	4.7	17000	26000	0.52
MYRM5	0.30	-	0.70	-	3.5	3.9	21000	33000	0.42
MYRM6	0.25	-	0.75	-	3.5	4.7	28000	45000	0.38
MYRM7	0.17	-	0.83	-	3.5	7.4	28000	43000	0.32
MYRM8	0.12	-	0.88	-	3.5	8.1	33000	52000	0.27
MYRF1	0.53	-	-	0.47	4.5	3.7	7800	12400	0.60
MYRF2	0.51	-	-	0.49	4.5	3.6	7900	17000	0.58
MYRF3	0.42	-	-	0.58	4.5	3.2	8700	14000	0.53
MYRF4	0.27	-	-	0.73	4.5	1.1	8700	15000	0.39
MYRF5	0.13	-	-	0.87	4.5	1.0	10200	17400	0.25

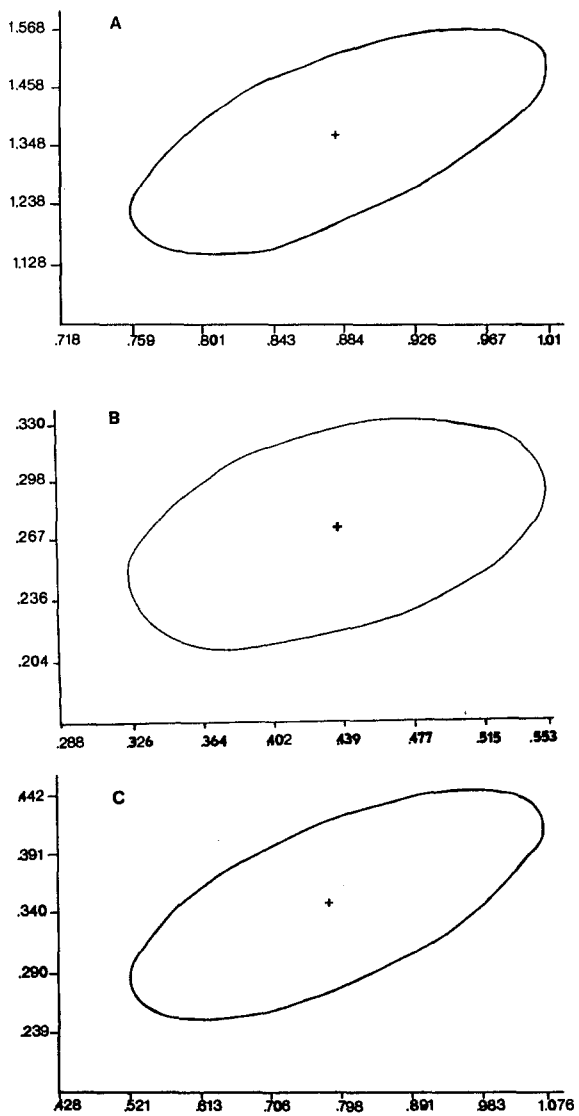


Figure 1
Joint confidence intervals for: A) myrcene-styrene;
B) myrcene-MMA; C) myrcene/p-fluorostyrene

TABLE 2

Reactivity Ratios				
M_1	M_2	r_1	r_2	$r_1 r_2$
Myrcene	Styrene	1.36	0.27	1.20
Myrcene	MMA	0.44	0.27	0.12
Myrcene	p-Fluorostyrene	0.79	0.35	0.28

For the myrcene-styrene copolymerization the product of r_1 and r_2 is greater than 1.0. While this is unusual it is not unique, particularly in cases where a diene is one of the comonomers. Several investigators have, in fact, obtained this result i.e. $r_1 r_2 > 1.0$ in the free radical copolymerization of butadiene and substituted butadienes with styrene (14-16) and in the copolymerization of acrylamide with styrene (17). For such copolymerizations $r_1 r_2 > 1$ means that relatively long sequences of like units are formed, in this case myrcene, as the growing polymer chain has a very strong preference for adding myrcene monomer regardless of terminus. The farther $r_1 r_2$ exceeds 1.0 the longer the sequences of like units that will be generated (18). For myrcene-styrene $r_1 r_2$ does not greatly exceed 1.0 and examination of the joint confidence limit reveals several possible values of r_1 and r_2 for which $r_1 r_2 < 1$ (of course there are several possible values of r_1 and r_2 where $r_1 r_2$ is significantly greater than 1 also). Therefore, given the experimental error involved, the history of diene-styrene copolymerizations and the fact that the product of the point estimates of r_1 and r_2 does not greatly exceed 1.0, we believe that the reactivity ratios are merely reflecting the strong preference of the growing polymer chains for myrcene monomer, i.e. the copolymerization results in this case are not so unusual as to warrant special explanation.

For the myrcene-MMA copolymerization the values of r_1 and r_2 obtained show that cross propagation reactions dominate i.e. each monomer radical has a preference for the other monomer; with the myrcene radical having a slightly greater preference for myrcene monomer than MMA radical has for MMA. The low value of $r_1 r_2$ does however, indicate some tendency towards alternation.

The myrcene/p-fluorostyrene also shows that each radical has a preference for the other monomer. However, the preference of the myrcene radical for myrcene is more marked in this case than in the myrcene-MMA copolymerization. The value of $r_1 r_2$ indicates that myrcene/p-fluorostyrene copolymers have more of a random nature than the other two copolymerizations examined in this study.

In order to estimate the average monomer sequence lengths for some of the copolymers synthesized in this study Pyun's equations (19) were applied. The results of these calculations are summarized

in Table 3.

TABLE 3
Monomer Mean Sequence Lengths

Polymer	M ₁	M ₂	Mole frac. M ₁ in Copolymer	μ ₁ ^b	μ ₂ ^c
MYRS1	Myr ^a	S	0.86	9.4	1.1
MYRS2	Myr	S	0.76	5.3	1.3
MYRS5	Myr	S	0.55	2.7	1.7
MYRS6	Myr	S	0.46	2.2	2.0
MYRS8	Myr	S	0.33	1.7	2.8
MYRS10	Myr	S	0.18	1.3	5.0
MYRS11	Myr	S	0.10	1.2	8.9
MYRM1	Myr	MMA	0.27	1.2	1.7
MYRM3	Myr	MMA	0.38	1.3	1.4
MYRM5	Myr	MMA	0.52	1.5	1.4
MYRM7	Myr	MMA	0.62	1.7	1.2
MYRM8	Myr	MMA	0.73	2.2	1.0
MYRF1	Myr	PFS ^d	0.70	2.8	1.2
MYRF2	Myr	PFS	0.58	2.1	1.3
MYRF4	Myr	PFS	0.39	1.5	1.5
MYRF5	Myr	PFS	0.25	1.3	2.1

a. Myr = Myrcene; b. μ₁ = average sequence length of monomer 1; c. μ₂ = average sequence length of monomer 2; d. PFS = p-fluorostyrene

The values given in Table 3 support statements made previously. For the myrcene-styrene copolymers the average sequence lengths indicate the preference of the growing polymer radicals for myrcene monomer. Myrcene in the feed must decrease to 0.29 mole fraction before the average sequence length of styrene exceeds that of myrcene. True, MYRS 11 shows long runs of styrene, but the myrcene comonomer is only 0.09 mole fraction of the feed in MYRS 11. Also, $r_2 = 0.88$ which is a relatively high value in its own right, and would eventually be expected to yield long runs of styrene given the appropriate feed concentrations.

The values obtained for the myrcene-MMA copolymers illustrate the tendency toward alternation that was predicted by the low r_1, r_2 value. The average sequence length of either monomer barely reaches 2.0. This indicates that the copolymers are not strictly alternating but come close to perfect alternation at some feed ratios. (MYRM 3 e.g.).

The values obtained for the myrcene/p-fluorostyrene copolymers indicate the more random nature of this copolymerization with average sequence lengths from 1.0 to 3.0. Again myrcene is the slightly more favored monomer.

Conclusions

Free radical copolymerization of myrcene with some common and uncommon monomers has been accomplished. The results of the copolymerizations were analyzed by a nonlinear least squares error-in-variables method and reactivity ratios were calculated. The reactivity ratios show myrcene to be a very reactive monomer with growing chains preferring to add myrcene monomer in all cases. This is particularly true for the myrcene-styrene copolymerization but less so for the myrcene/p-fluorostyrene comonomers and much less so for the myrcene-MMA monomer pair, where there is near alternation of the monomers with only a slight preference for myrcene monomer. The data set for the p-fluorostyrene copolymerization is small, only five points. This is partially due to the expense involved in obtaining the p-fluorostyrene. However, further studies are underway with more data points being gathered. But, the data presented for the p-fluorostyrene is of fairly high quality and the values given for r_1 and r_2 are believed to be reasonably accurate.

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