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Physical Properties of Copolymers of Styrene and α -Olefins

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Copolymerizations of styrene and α -olefins such as propylene, butene-1, pentene-1, heptene-1 and decene-1 have been carried out with organo-metallic compound catalysts in order to study physical properties, copolymerizability and crystallizability. It is concluded, as a result that the apparent copolymerizability of styrene monomer to the opponent comonomers may increase in accordance with increase of the length of side chains of the comonomers owing to the difference in their steric hindrance. In the case of copolymerization between styrene and hexene-1, each constituent of the monomers was distributed most randomly each other. The product of monomer reactivity ratios, $r(\text{Styrene}) \times r(\alpha\text{-Olefin})$ was found to approximately equal to 1 in all of the copolymerizations investigated. It is expected that by the copolymerization with heptene-1 or decene-1 some adverse physical properties of crystalline polystyrene such as the brittleness and low heat-drawability may be improved without much lowering of its melting point.

INTRODUCTION

Many kinds of crystalline polyolefins have been developed by making use of organo-metallic compound catalysts. As one example, isotactic polystyrene is known to have a high melting point of about 230°C and to be able to give a fiber of high tensile strength, for example 2~5 g/d by melt spinning process. It has further many favorable properties such as low density, excellent elastic properties, high Young's modulus, and good heat-resistance and so on. However, as adverse property, it is rather brittle at room temperature and the drawing process after melt spinning is usually somewhat difficult. In viewing those favorable and unfavorable properties of isotactic polystyrene, we have studied copolymerization between styrene and linear α -olefins by the use of organo-metallic compound catalysts. The copolymerization of propylene and styrene with Ziegler-Natta type catalysts have been widely researched^{1,2,3,4}. However, the physical properties of the resultant copolymer have not been investigated in detail. Moreover, copolymerization of styrene and other linear α -olefin with long side group such as heptene-1 or decene-1 has not been examined as yet. By block copolymerization techniques, it is possible to prepare a copolymer having many favorable properties such as not expected from simple mixing of two homopolymers, even in a case that two homopolymers are not compatible each other. Further scope for combination is provided by the fact that even when block copolymers are coexistent with some homopolymers or statistical copolymers, incompatibility phenomena such as demixing, embrittlement and so on, are frequently absent or reduced. On the other hand, it is also interesting to see how the copolymerizability of styrene changes by incorporating

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α -olefins with different steric hindrance and to research how the distribution of styrene composition and crystallizability of copolymer are dependent on the copolymerization conditions.

EXPERIMENTAL AND DISCUSSION

1. Copolymerization

Monomer reactivity ratios for styrene and α -olefins such as butene-1, pentene-1, heptene-1 and decene-1 were determined by use of data from a series of batch copolymerizations of low conversion. The graphical procedure of Fineman and Ross⁵⁾ was employed to evaluate the relative copolymerizability of each series of monomers. The composition of the copolymers obtained was estimated from absorption ratios of infrared spectra.

Copolymerization of styrene and propylene. The four kinds of catalyst systems such as $\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3\text{-}n(\text{C}_4\text{H}_7)_3\text{N}$, $\text{VCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3$, $\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and $\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)\text{Cl}_2\text{-}n(\text{C}_4\text{H}_9)_3\text{N}$ were utilized. The catalyst was added into a flask of 1 liter containing *n*-heptane as diluent under atmosphere of nitrogen, and after controlling the temperature at 50°C, monomers were fed in two following manners. The one was that after bubbling of propylene gas for a predetermined period at the rate of 100 ml/min., 100 ml. of styrene monomer was added into the reaction mixture. By this procedure, a copolymer of two stepwise block type,

Table 1. Copolymerization of styrene and propylene.

Poly(propylene-*b*-styrene)

Sample No and catalysts employed	Atactic polymer in crude polymer ^{a)} Wt. %	St. homo polymer in crude polymer ^{b)} Wt. %	Copolymer in crude polymer ^{c)} Wt. %	Mol % of styrene in the copolymer ^{d)}
$\text{TiCl}_3\text{-AlEt}_3\text{-}n\text{Bu}_3\text{N}$				
200	2.7	13.2	84.1	4.3
400	1.7	85.0	13.3	6.6
500	1.4	27.4	71.2	5.0
600	1.3	90.5	8.2	10.8
2700	0.8	60.5	38.7	1.4
$\text{VCl}_3\text{-AlEt}_3$				
2400	8.6	90.4	1.0	0.02
2500	8.8	61.0	30.2	2.1
$\text{TiCl}_3\text{-AlEt}_2\text{Cl}$				
1300	78.4	15.5	6.1	1.1
1900	56.3	40.5	3.2	6.2
$\text{TiCl}_3\text{-AlEtCl}_2\text{-}n\text{Bu}_3\text{N}$				
1600	56.0	27.5	16.5	2.6
1800	79.0	15.7	5.3	3.2

a) Soluble part in acetone

b) Insoluble part in *n*-nonane

c) Soluble part in *n*-nonane

d) Estimated by infrared spectrum technique

Physical Properties of Copolymers of Styrene and α -Olefins

Table 2. Copolymerization of styrene and propylene.

 Poly(styrene-*b*-[propylene-*co*-styrene])

Sample No and catalysts employed	Atactic polymer in crude polymer ^{a)} Wt. %	St. homo polymer in crude polymer ^{b)} Wt. %	Copolymer in crude polymer ^{c)} Wt. %	Mol % of styrene in the copolymer ^{d)}
TiCl ₃ -AlEt ₃ - <i>n</i> Bu ₃ N				
100	1.6	91.5	6.9	33.3
700	1.3	90.3	8.4	41.9
800	3.0	90.0	7.0	54.4
900	3.8	88.5	7.7	15.0
TiCl ₃ -AlEt ₂ Cl				
1400	38.6	37.1	24.3	0.01
TiCl ₃ -AlEtCl ₂ - <i>n</i> Bu ₃ N				
1700	94.7	4.0	1.3	9.8

a), b), c), d) Explained in Table 1.

poly(propylene-*b*-styrene), was to be obtained. The another was that after styrene monomer was polymerized for a period, propylene gas was bubbled into the flask for a predetermined period. By this process a random type copolymer, poly(styrene-*b*-[propylene-*co*-styrene]), was synthesized. The resultant polymers were isolated by use of methanol containing hydrochloric acid, and purified by extracting with methanol and dried. The products obtained were first extracted with acetone to remove the atactic polystyrene of low molecular weight. The results of the extraction are shown in Table 1 and 2, from which it is known in the case of alkyl aluminium catalyst systems, a great part of the crude polymers consists of atactic polystyrene, probably due to cationic polymerization⁶⁾. It may come to a conclusion that alkyl aluminium halide catalyst systems are effective to increase stereoregularity of propylene component⁷⁾, but not to increase the content of styrene units and its regularity in polymerized products.

Copolymerization of styrene and butene-1. The copolymerization was carried out in an autoclave of 500 ml. capacity to determine monomer reactivity ratios between styrene and butene-1 at 60°C and under nearly an atmospheric pressure, employing TiCl₃-AlEt₃ catalyst (Al/Ti molar ratio of 2.0). From the data of Fig. 1, the monomer reactivity ratios for butene-1 and styrene were evaluated as 5.51 for $r(\text{Bu-1})$ and 0.198 for $r(\text{St})$, respectively. These values indicate that polymerization rate is much greater for butene-1 than for styrene, and the resultant copolymer is composed primarily of repeating units of butene-1 with a random insertion of styrene unit.

Copolymerization of styrene and pentene-1. Sixteen runs of copolymerization were carried out for 3 hrs. at 50°C in a similar way as described above, changing monomer mixture ratio between styrene and pentene-1. TiCl₃-AlEt₃ catalyst system was used and the molar ratio of Al/Ti was 1.5 and the concentration

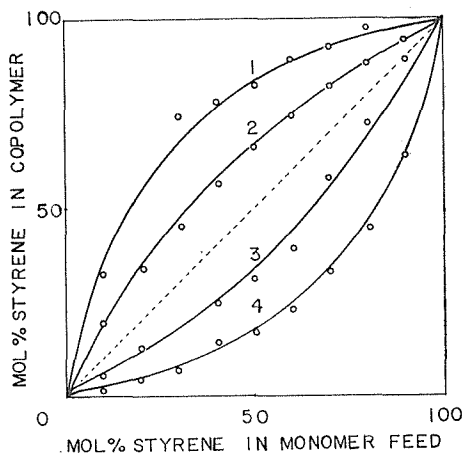


Fig. 1. Monomer-polymer composition curves.

1. Styrene-Decene-1, 2. Styrene-Heptene-1,
3. Styrene-Pentene-1, 4. Styrene-Butene-1.

of TiCl_3 was 0.108 mol/l throughout the runs. The reactivity ratios, $r(1\text{-Pe})$ and $r(\text{St})$ were evaluated as 1.51 and 0.448 respectively, from which it might be considered that monomers of styrene and pentene-1 would be combined each other at random and the constituent of pentene-1 being rich in the molecular sequence.

Copolymerization of styrene and heptene-1. The melting point of isotactic polyheptene-1 is known to be very low as about -20°C , hence it is expected to produce a copolymer of relatively less brittleness by copolymerizing small amount of the monomer with styrene. Into a 120 ml. quantity of the mixture of triethyl aluminium-titanium trichloride ($\text{Al/Ti}=2.5$ in molar ratio) and *n*-heptane, was fed a monomer mixture of styrene and heptene-1 and polymerized at 70°C for 5 hrs. in the same fashion as in the preceding experiment. The polymerization yield was not high, particularly it was very low in the case of monomer mixture of 1/1 molar ratio. The copolymerization rate and copolymerizability of styrene monomer are generally expected to increase as the side chain of opponent comonomer becomes longer. As expected, it is recognized from Fig. 1 that styrene content in the polymerized product appears in a range above the theoretical straight line when $r_1 \times r_2 = 1$, $r_1 = r_2 = 1$. From the figure the monomer reactivity ratios was also calculated as, $r(\text{St})=1.92$, and $r(1\text{-Hep})=0.51$.

Copolymerization of styrene and decene-1. A mixture of styrene and decene-1 was polymerized at 70°C for 4 hrs., using catalyst system of $\text{TiCl}_3\text{-AlEt}_3$, where Al/Ti molar ratio was 2.0 and the concentration of TiCl_3 was 0.054 mol/l. By the same procedure, $r(1\text{-De})$ and $r(\text{St})$ were determined as 0.16 and 5.00, respectively. Monomer reactivity ratios and their product were summarized in Table 3.

Table 3. Monomer reactivity ratios for copolymerization of styrene and α -olefins.

Comonomer	r_1 (Styrene)	r_2 (α -Olefin)	$r_1 \cdot r_2$
Propylene ¹⁾	0.12	7.70	0.92
Butene-1 ²⁾	0.20	5.51	1.10
Pentene-1 ³⁾	0.45	1.51	0.68
Heptene-1 ⁴⁾	1.92	0.51	0.98
Decene-1 ⁵⁾	5.00	0.16	0.80

¹⁾ according to I. Hayashi³⁾.

²⁾ 60°C, Al/Ti=2.0

³⁾ 50°C, Al/Ti=1.5

⁴⁾ 70°C, Al/Ti=2.5

⁵⁾ 70°C, Al/Ti=2.0

2. Fractionation by Solvent Extraction

The copolymerized crude products are thought to be composed of macromolecules of different components, in which homopolymers as well as copolymers from each monomer may exist. In order to confirm the presence of real copolymer and to investigate the composition of each component, the crude products were fractionated by progressive extractions with different kinds of solvents. The extraction was carried out by a Soxhlet type extractor with vapor jacket. A series of hydrocarbons of different boiling points, and ether, methyl ethyl ketone and so on were used as solvent for the extraction. The dissolved polymer was precipitated and washed with propyl alcohol, and the insoluble residue was washed repeatedly with alcohol. Each fraction thus obtained was molded into a film at a favorable temperature above its melting point to investigate physical and mechanical properties.

Extraction of copolymer of styrene and propylene. The copolymerized product of styrene and propylene by the two step technique (poly(propylene-*b*-styrene)) was fractionated by the progressive extractions with different kinds of solvents. The fractionation by extraction of polypropylene with boiling hydrocarbons of increasing boiling points is reported by G. Natta⁶⁾ to separate mainly according to isotacticity, whereas isotactic polystyrene is expected to be insoluble in any boiling hydrocarbons such as *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane and *n*-nonane. Therefore, it may be possible to remove isotactic styrene homopolymer from the products and further to fractionate the remaining products according to the composition by progressive extraction with a series of hydrocarbons of increasing boiling temperature. After atactic polystyrene was first removed from the product as a soluble part in acetone, insoluble residue was divided into two parts by extracting with boiling *n*-nonane of about 150°C. The *n*-nonane-insoluble part was confirmed to be isotactic polystyrene by infrared spectrum, and the soluble part was concluded by the following experiment to be a real copolymer of styrene and propylene. All results of the extraction are summarized in Table 1 and 2. The *n*-nonane-soluble

Table 4. Fractionation of propylene styrene copolymer prepared by $\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3$, by progressive extraction of hydrocarbons with different boiling points.

Fraction No.	Extraction B.p. °C	Extracted Wt %	Cont. of St. Mol %	D_{995}/D_{974}
2701	32	2.99	3.32	0.512
2702	66	7.70	2.70	0.665
2703	71	2.49	1.20	0.791
2704	75	2.56	0.72	0.861
2705	80.5	1.12	0.78	0.872
2706	86	0.71	0.95	0.904
2707	93.5	0.90	1.32	0.943
2708	98	3.01	1.51	1.129
2709	95	0.54	1.80	0.982
2710	103	30.24	0.52	0.969
2711	106	1.35	1.01	0.954
2712	109.5	11.80	2.50	0.924
2713	115	20.49	3.43	0.956
2714	117	4.21	0.10	0.991
2715	121	5.79	0.34	0.934
2716	124	2.15	0.95	0.999
2717	135	1.35	0.97	0.983

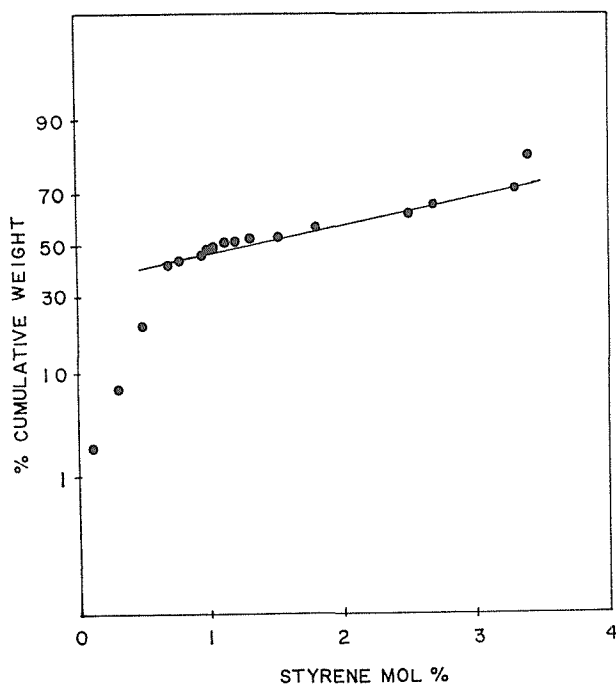


Fig 2. The distribution of composition in styrene-propylene copolymer prepared with $\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_2$ catalyst,

part has been extracted progressively with distilled fractions of ligroin and kerosine. The results are shown in Table 4. It is shown from the table that all the fractions contain always styrene component which is distributed ununiformly. This indicates that the crude product is composed of copolymer and styrene homopolymer, but does not contain propylene homopolymer. In Fig. 2, the cumulative weight fraction for sample No. 2700 is plotted against styrene content on probability paper from the data of Table 4. It is seen in the figure that experimental points comprise a straight line in the range of cumulative weight fraction of about 0.5. It must be indicative of that the distribution of styrene composition in the copolymer is given approximately as a normal distribution. The results for other copolymers which were extracted in the same way by hydrocarbons such as *n*-heptane, methyl cyclohexane and *n*-octane at their boiling points, are shown in Fig. 3 and 4, which indicate also normal distribution of styrene component. The slopes of the straight lines in the figures are dependent not only on monomer species but also catalyst systems. Hence, it may imply that uniformity of the distribution of styrene composition in

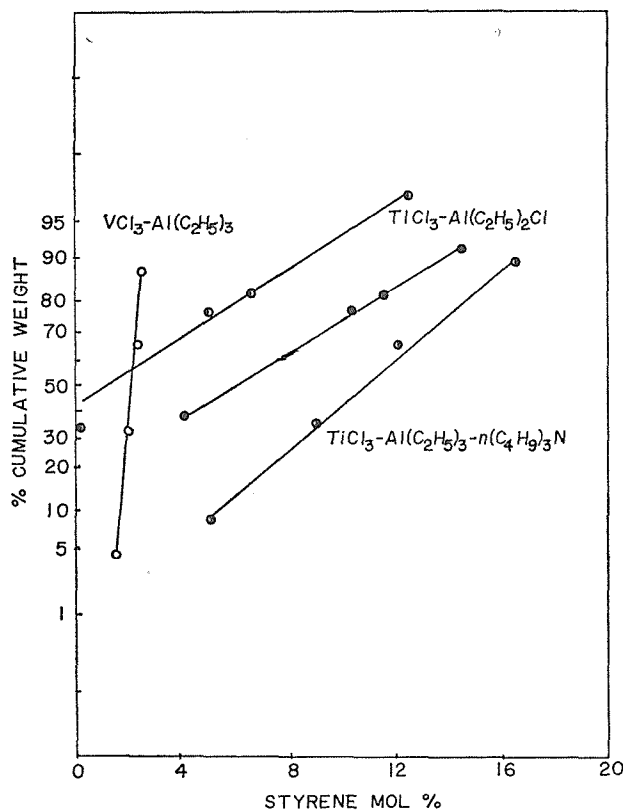


Fig. 3. The distribution of composition in styrene propylene copolymers prepared by different catalyst systems.

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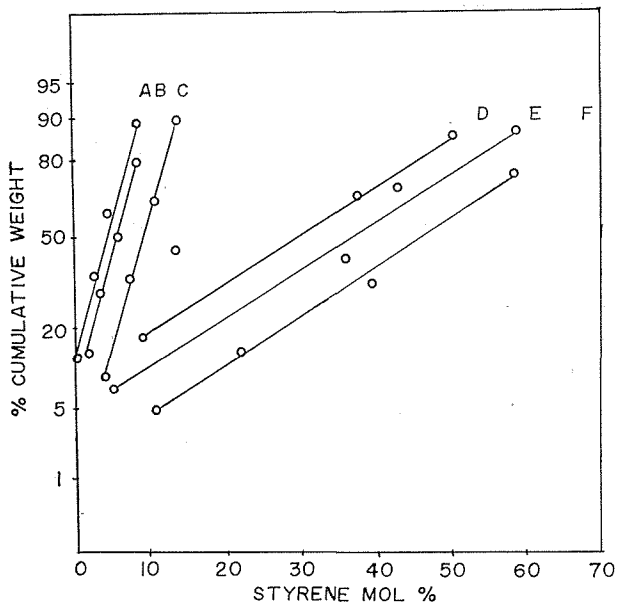


Fig. 4. The distribution of composition in styrene-propylene copolymer prepared by $\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3$.
 A, B, C = Poly(propylene-*b*-styrene)
 D, E, F = Poly(styrene-*b*-[propylene-*co*-styrene])

copolymer depends on monomer species as well as catalyst systems. It is recognized that the composition distribution of, for example, the block copolymer, poly(propylene-*b*-styrene) becomes to be more uniform in the order of from $\text{TiCl}_3\text{-AlEtCl}_2\text{-}n\text{Bu}_3\text{N}$ to $\text{TiCl}_3\text{-AlEt}_2\text{Cl}$, $\text{TiCl}_3\text{-AlEt}_3$, and $\text{VCl}_3\text{-AlEt}_3$.

Extraction of copolymer of styrene and butene-1. The homopolymer of butene-1 is essentially insoluble in toluene of 45°C, while polystyrene is easily soluble in it but insoluble in boiling methyl cyclohexane. A crude product treated with acetone was next extracted with methyl cyclohexane at its boiling temperature 101°C to remove styrene homopolymer. Thus a series of fractions of different styrene contents was isolated as methyl cyclohexane extract and further examined. Among them, the fraction of minimum styrene content, 7.2 mol %, was confirmed to be completely soluble in toluene of 45°C. Hence, all fractions obtained were thought to be soluble in it. Therefore, it seems to indicate that the polymer soluble in methyl cyclohexane is a copolymer rather than a mixture of homopolymers of both components.

Extraction of styrene and pentene-1 copolymer. A series of crude products shown in Table 5 were first extracted with methyl cyclohexane to remove styrene homopolymer as insoluble residue. The isolated products without styrene homopolymer were then extracted with ether. A homopolymer of pentene-1 is

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Table 5. Copolymerization of styrene and pentene-1 and extraction at boiling points of various solvents.

St./Pe-1. monomer feed mixture	Yield	Styrene mol %	Insoluble part in methyl cyclo- hexane (styrene homo polymer)	Soluble part in methyl cyclohexane			
				Soluble part in ether		Insoluble part in ether	
Molar %	Weight %		Weight %	St. mol %	Weight %	St. mol %	Weight %
19.6/80.4	39.3	11.2	21.8	11.8	21.5	10.6	56.7
32.8/67.2	18.5	22.0	17.8	19.2	32.1	24.8* ¹⁾	50.1
44.7/55.3	2.11	—	71.8	—	—	—	—
55.0/45.0	28.1	31.0	48.2	33.2* ²⁾	15.6	29.7	35.2
64.7/35.3	28.8	28.7	75.5	29.8* ³⁾	13.9	27.5	10.6
82.3/17.7	23.0	36.3	78.0	36.6	10.4	37.0	11.6
90.0/10.0	4.93	66.8	88.6	67.9	4.5	65.8	6.9

Sample	M.E.K.**-soluble		M.E.K.-insoluble	
	Weight %	St. mol %	Weight %	St. mol %
*1)	23.6	25.2	76.4	20.9
*2)	55.7	34.7	44.3	31.8
*3)	20.5	36.7	79.6	31.7

**) Methyl ethyl ketone

generally soluble in ether. Hence, ether-insoluble parts must be a real copolymer of styrene and pentene-1. However, styrene contents in the both parts, soluble and insoluble in ether were almost the same. It may indicate that the ether-soluble part also contains a real copolymer. To further elucidate this fact, samples designated as *1), *2), and *3) in Table 5 were extracted with methyl ethyl ketone which could dissolve polystyrene, particularly atactic polystyrene, but not dissolve poly-pentene-1. The data of Table 5 indicate that the styrene contents are approximately equivalent in the both parts, soluble and insoluble in the solvent. It is therefore considered that both components of styrene and pentene-1 may be uniformly distributed in the random copolymer, which may be supported from the results of examining the monomer reactivity ratios shown in Table 3.

Extraction of copolymers of styrene and heptene-1 and styrene and decene-1. In these cases homopolymer of styrene could be removed from the crude polymerized product by extracting with *n*-heptane, and moreover, ether was found to be the most convenient solvent to remove homopolymers of heptene-1 and decene-1. The fact that any copolymerized crude product of styrene and α -olefin contained always isotactic styrene homopolymer would lead to a conclusion that the active species to promote preferentially growing of styrene chain were present in the system of complex catalyst examined during the copolymerization process.

3. Stereoregularity and Crystallinity

Employing organo-metallic compound catalysts, it would be expected to give a series of cocrystalline copolymers from styrene and α -olefins. The effect of each composition on the stereoregularity or the crystallizability of the copolymer will be discussed from the measurements of infrared spectrum, X-ray diffraction, melting point and density. The infrared spectra of a copolymer fraction of styrene and propylene isolated by the aforementioned extraction showed a characteristic band, 995 cm^{-1} of isotactic polypropylene and 618 and 583 cm^{-1} of isotactic polystyrene. The apparent isotacticity calculated from the absorption ratio D_{974}/D_{995} , after

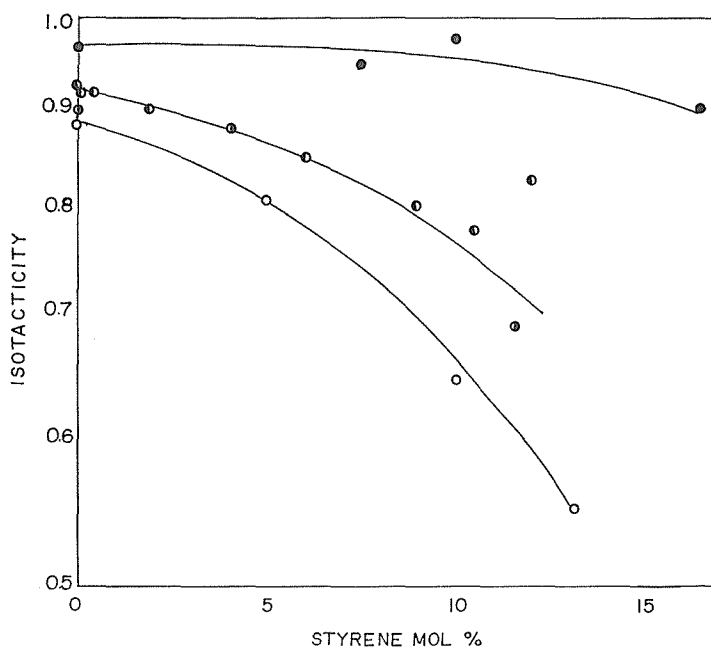


Fig. 5. The influence of composition on an apparent isotacticity of propylene sequence in styrene-propylene copolymer.

● Fraction at 140-150°C ◐ Fraction at 115-120°C
 ◑ Fraction at 100°C ○ Fraction at 95-98°C

J.P. Luongo⁹⁾, was plotted against styrene mol % in Fig. 5, from which it was recognized that isotactic propylene sequence was generally present in a series of copolymers soluble in hydrocarbons and the apparent isotacticity was dependent on the content of styrene component. On the other hand, the presence of isotactic and atactic sequence of styrene constituent could be confirmed by 618 and 583 cm^{-1} bands of isotactic polystyrene and 543 cm^{-1} band characteristic of atactic polystyrene, and regularity of the isotactic sequence was found to be minimum at about 20 mol % of styrene from examining of intensities of the D_{618}/D_{543} and D_{583}/D_{543} (Fig. 6). As shown in Fig. 6, the similar result could be obtained also for copolymers of

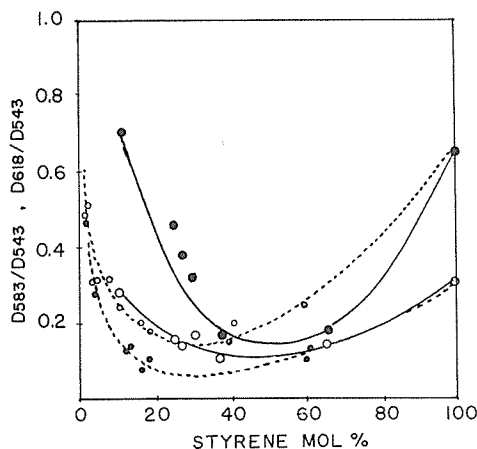


Fig. 6. Correlation between D_{618}/D_{543} and D_{583}/D_{543} of infrared spectra and styrene composition in styrene-propylene and styrene-pentene-1.

— Styrene-pentene-1
 ● D_{583}/D_{543} ○ D_{618}/D_{543}
 --- Styrene-propylene
 ⊙ D_{583}/D_{543} ⊙ D_{618}/D_{543}

styrene and pentene-1. The infrared spectrum of styrene and butene-1 copolymer was characterized by an absorption band at 560 cm^{-1} . It is supposed that the band of 543 cm^{-1} associated with vibration of phenyl group would shift to 560 cm^{-1} by the copolymerization. Examining X-ray photographs of drawn and annealed films of these samples, it was found that styrene and α -olefin copolymers obtained, generally had crystallizability and it diminished as styrene content increased. In fact, X-ray scanning curves showed the lowering of crystallizability according as the increase of styrene content. The measurements of density and melting

Table 6. Melting point depression with increasing styrene content in the copolymer of styrene and propylene, extractable by higher boiling hydrocarbons, such as *n*-octane and *n*-nonane.

Sample No.	Mol % of styrene	Observed melting point ^{a)} °C	Calculated melting point ^{b)} °C
2540	1.9	165.5	173.0
441	2	164.2	172.9
531	3.5	160.5	170.7
541	10.5	154.0	159.6
741	42	—	105.4
141	57.5	—	74.2
851	66.5	—	51.3

^{a)} Dilatometric method ($1^\circ\text{C}/\text{min.}$) or differential thermal analysis ($6^\circ\text{C}/\text{min.}$) was employed.

^{b)} These values were obtained from the Flory's theoretical equation, using the values of $\Delta H=2600\text{ cal/mol}$, and $T_m^0=449^\circ\text{K}$.

point (Table 6) of styrene-propylene copolymer also support this conclusion, and the crystallinity X_c , of the copolymers obtained from the following formula will reveal to become negligible as styrene content approaches 15 mol %, as shown in Fig. 7,

$$X_c = (V_a - V) / V_a - V_c$$

where, V_a represents the specific volume of the copolymer in complete amorphous state which is assumed to be equal to weight average of the specific volumes of

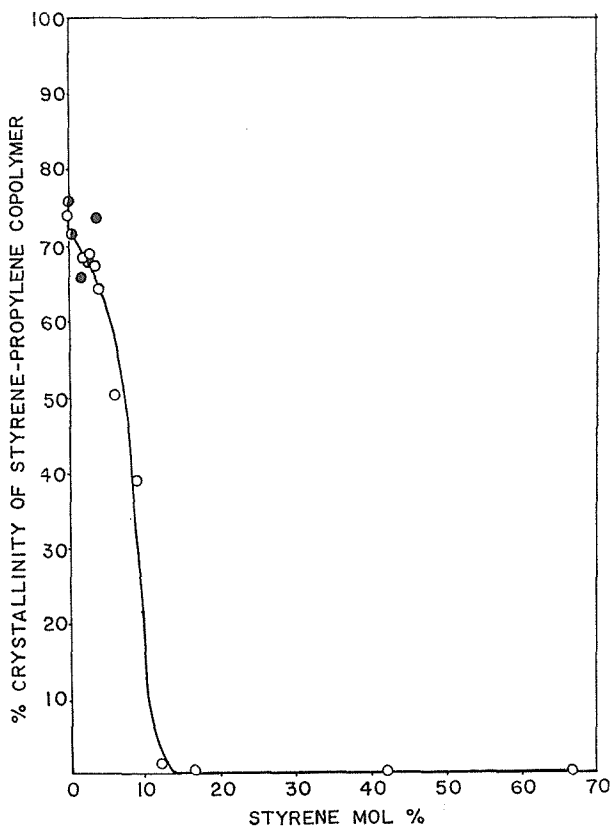


Fig. 7. Effect of composition on crystallinity by density measurement of copolymer of styrene and propylene.
 (●) TiCl₃-AlEt₂Cl (●) VCl₃-AlEt₃ (○) TiCl₃-AlEt₃-nBu₃N

the homopolymers of both components in amorphous state, V_c a specific volume of the homopolymer of propylene in the completely crystalline state and V_a specific volume of the copolymers observed at 30 °C in a density gradient column composed of ethylene glycol and propyl alcohol. From the results described above, it must be concluded that, although the crystallizability of these copolymers is dependent on the content of each composition, the copolymers of styrene examined may possess a tendency to form cocrystalline copolymer.

4. The Mechanical Properties

The mechanical properties of all copolymers obtained were studied. Test pieces of the molded films of 10 mm in length and 1.0 mm in width were examined by a tensile tester of Instron type at the cross head speed of 10 mm/min. at 20°C and 65% R.H. As mentioned above, a block copolymer of high styrene content and of high crystallizability could not be obtained by use of propylene or butene-1 as comonomer. On the other hand, copolymers of high styrene content could be obtained by use of pentene-1, heptene-1 or decene-1. The results for copolymers of styrene and pentene-1, heptene-1 and decene-1 are summarized in Table 7. It is ascertained from the table that by a little addition of heptene-1 or decene-1 the elongation at room temperature considerably increases, compared with that of styrene

Table 7. The mechanical properties of copolymers of styrene and α -olefins.

Comonomer	Mol % of styrene	Tensile strength kg/mm ²	Elongation %	Young's modulus kg/mm ²
Amorphous polystyrene		3.97	4.0	212
Crystalline polystyrene		1.26	3.8	142
Pentene-1	12.5	0.389	552	11.2
	23.6	0.372	496	14.6
	34.8	0.073	91.1	6.21
	57.5	1.04	1.53	37.2
	71.5	0.414	5.9	13.1
	89.8	0.74	4.23	35.3
Heptene-1	80.1	0.866	59.8	12.5
	88.2	0.525	11.9	14.0
Decene-1	81.8	0.402	112.2	11.1
	88.7	0.341	37.3	9.4
	92.4	0.927	24.8	18.8

homopolymer, while Young's modulus decreases. However, the tensile strength of the copolymers seems to be somewhat low. But it might be possible to combine high tensile strength and large elongation in a range of the lower comonomer content than those examined here. The dimensional stability of the samples at elevated temperatures is shown in Fig. 8. The longitudinal dimensions of molded films of 3 cm in length and about 0.2 mm² in cross-sectional area were measured with increasing of temperature in a silicon oil bath under the tension of 0.1 or 0.01 kg/mm² the temperature being increased at the rate of 1°C/min. The dimensional stability of crystalline styrene homopolymer is most excellent so that it does not indicate much shrinkage up to the temperature of 230°C, which may be attributed to the high melting point and high crystallinity. In the case of the styrene decene-1 copolymer which contains 7.6 mol % of decene-1, as shown in No. 5 of Fig. 8, it is recognized that the copolymer has excellent dimensional stability against temperature, in

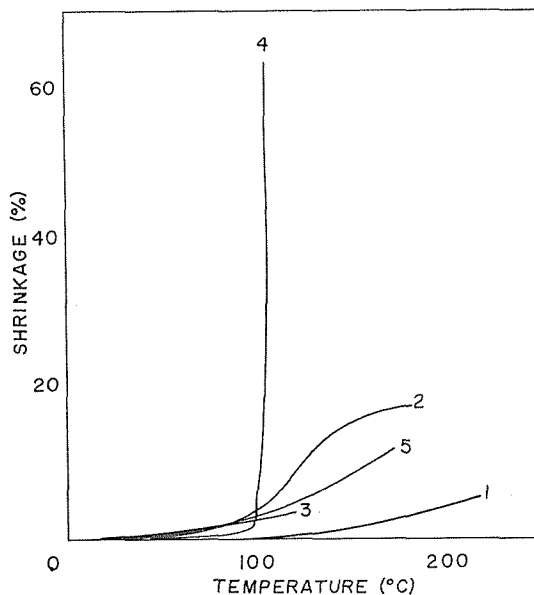


Fig. 8. The shrinkage-temperature curves for styrene α -olefin copolymers.

1. Crystalline polystyrene, 2. Styrene-propylene (42.4 mol %), 3. Styrene-butene-1 (41.2 mol %), 4. Styrene-heptene-1 (80.1 mol %), 5. Styrene-decene-1 (92.4 mol %), () shows content of styrene in copolymer.

spite of the low melting point of polydecene-1, near about 20°C. As a conclusion, it is supposed that the brittleness of isotactic polystyrene may be improved by incorporating a little amount of α -olefins such as decene-1 and heptene-1 by the copolymerization.

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REFERENCES

- (1) H. Hagemeyer, *Modern Plastics*, **39**, 157, (1962).
- (2) A. Gandini and C. Heinen, *Makromol. Chem.*, **54**, 126, (1962).
- (3) I. Hayashi and R. Ichikawa, *J. Chem. Soc. of Japan*, **66**, 102, 108, (1963).
- (4) N. Ashikari, T. Kanemitsu, K. Yanagisawa, K. Nakagawa, H. Okamoto, S. Kobayashi and A. Nishioka, *J. Polymer Sci.*, **A2**, 3009, (1964).
- (5) M. Fineman and S. D. Ross, *J. Polymer Sci.*, **5**, 269, (1950).
- (6) S. Murahashi, S. Nozakura, and K. Hatada, *Bull. Chem. Soc., Japan*, **34**, 939, (1961).
- (7) H.W. Coover, Jr. and F.B. Joyner, *J. Polymer Sci.*, **A3**, 2407, (1965).
- (8) G. Natta, *J. Polymer Sci.*, **34**, 531, (1959).
- (9) J.P. Luongo, *J. Appl. Polymer Sci.*, **3**, 302, (1960).