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Block and Bigraft Copolymers by Carbocation Polymerization*

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ABSTRACT

The recent observation that the rate of methylation of t-BuCl by Me_3Al is several orders faster than that of t-BuBr, which in turn is much faster than that of t-BuI, provides the basis of a new synthetic method for the preparation of block and bigraft copolymers. This presentation concerns the synthesis and characterization of the first well-defined block and bigraft copolymers produced by the carbenium ion mechanism i.e., poly(styrene-b-isobutylene), poly[(ethylene-co-propylene)-g-styrene-g-isobutylene)], and poly[(ethylene-co-propylene)-g-styrene-g-α-methylstyrene)]. The synthesis of the block copolymers involved three key steps: 1) the synthesis of a chlorobrominated alkane initiator, 2) the selective initiation of styrene polymerization by the chlorobrominated alkane in conjunction with alkylaluminum halide under conditions of no chain transfer, and 3) selective initiation of isobutylene polymerization by the polystyrene-Br in conjunction with alkylaluminum halide. Selective solubility, DSC, and GPC

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*In the authors' absence, the paper was delivered by Dr. Patricia Dreyfuss.

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data indicate pure block copolymer. The effect of temperature on the intrinsic viscosity of poly(styrene-b-isobutylene) exhibited peculiarities characteristic of block copolymers. The bigraft was synthesized by chlorobrominating an ethylene-propylene copolymer and selectively initiating first the polymerization of styrene and subsequently that of α-methylstyrene or isobutylene by the chlorobrominated copolymer plus an alkylaluminum compound.

INTRODUCTION

The recent discovery that alkylaluminum/alkyl halide combinations, e.g., Et_2AlCl/t-BuCl, are excellent initiator systems for the cationic polymerization of a large variety of olefins [1, 2] has given rise to vigorous fundamental and development studies in the United States [3, 4] and in Europe [5, 6]. In particular, the Et_2AlCl/t-BuCl system initiates the rapid polymerization of styrene to a very high molecular weight product and, importantly, the polymerization proceeds in the absence of chain transfer. The latter circumstance led to the development of novel graft copolymers [7] and, more recently, to the development of block and bigraft copolymers, the subject of this presentation.

The discovery of the principle that led to the first carbenium ion synthesis of block and bigraft copolymers was made during our fundamental studies concerning the effect of the nature of the tertiary butyl halide on the rate of methylation by Me_3Al, i.e.,

$$Me_3Al + t\text{-}BuX \rightarrow t\text{-}BuMe + Me_2AlX$$

where X = Cl, Br, and I [8].

Significantly, the rate of methylation of t-BuCl by Me_3Al in methyl chloride diluent was found to be many orders of magnitude larger than that of t-BuBr. Table 1 shows the findings.

SYNTHESIS AND CHARACTERIZATION OF POLY(STYRENE-b-ISOBUTYLENE)

Synthesis

It was theorized that the huge difference in methylation rates shown in Table 1 could be exploited in the synthesis of a block

TABLE 1. Rates of Alkylation of t-Butyl Halides with Trimethylaluminum at -40°C

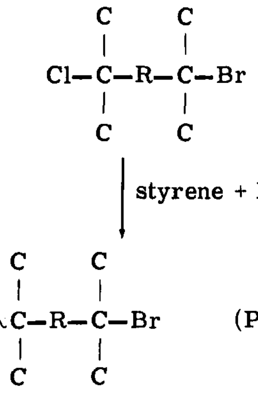
	k[liter/(mole)(sec)] × 10^6			
t-BuX	MeCl	MeBr	MeI	Cyclopentane
t-BuCl	>10^9 [a]	4100	2000	1.2
t-BuBr	13000	1800	100	0.7[b]
t-BuI	75[c]	15[c]	3.2[c]	0.005[b]

[a] Calculated from the observed rate at -80°C, assuming an activation energy of ~10 kcal/mole.

[b] Calculated from the measured rates in the temperature range -0 to +50°.

[c] Calculated from the measured rates in the temperature range -20 to +20°.

copolymer, for example, poly(styrene-b-isobutylene). The plan was to synthesize a small molecule containing both a tertiary chloride and a tertiary bromide, and using it in conjunction with an alkylaluminum compound to initiate the polymerization of a monomer first only from the chloride site and subsequently to initiate the polymerization of another monomer from the bromine site. The concept using styrene and isobutylene as the two monomers may be schematized as follows:

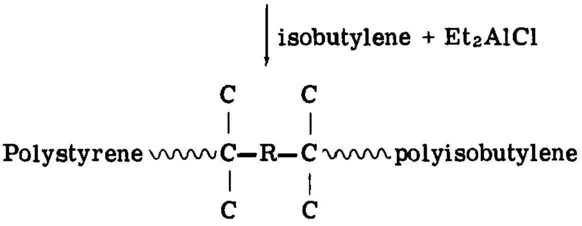


1. Synthesis of $\mathrm{Cl{-}\overset{C}{\underset{C}{C}}{-}R{-}\overset{C}{\underset{C}{C}}{-}Br}$ R = $-(\mathrm{CH_2})_3-$

$$\downarrow \text{styrene + Et}_3\text{Al}$$

2. Polystyrene$\sim\!\sim\mathrm{\overset{C}{\underset{C}{C}}{-}R{-}\overset{C}{\underset{C}{C}}{-}Br}$ (PSt-Br)

3. Remove unreacted chlorobromo initiator



$$\Big\downarrow \text{isobutylene} + Et_2AlCl$$

4. $$\text{Polystyrene}\sim\sim\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}\text{—R—}\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}\sim\sim\text{polyisobutylene}$$ (PSt-b-PIB)

For this plan to succeed it was essential to work out conditions under which sequential initiation can be achieved. Model studies and other experiments indicated that 2-chloro-6-bromo-2,6-dimethylheptane (ClBrDMH) in conjunction with Et_3Al or Et_2AlCl was suitable for this purpose. For example, about 50% of the chlorine in this chlorobrominated alkane can be substituted before any bromine loss using Et_3Al in CH_3Cl at -70°C.

Fundamental studies had shown previously that the polymerization of styrene coinitiated, for example, by Et_3Al proceeds essentially free of chain transfer. This background information was needed for the "clean" synthesis of polystyrene possessing a terminal tertiary bromine (PSt-Br).

Again, model studies indicated that the addition of ClBrDMH to a charge of styrene and Et_3Al in C_2H_5Cl at -80°C readily gave PSt-Br of $\overline{M}_n = 20{,}000$, suitable for the subsequent isobutylene polymerization step.

Prior to the isobutylene polymerization, unreacted ClBrDMH had to be removed. Residual ClBrDMH initiator, in conjunction with the subsequently added alkylaluminum compounds, might give homopolyisobutylene and thus contaminate the block copolymer. Thus unreacted ClBrDMH was removed by dissolving the PSt-Br in CH_2Cl_2, filtering (to remove some aluminum oxides which arose during the quenching of the styrene polymerization with cold methanol), and pouring the CH_2Cl_2 solution into an excess of methanol. The precipitated PSt-Br was washed several times with methanol and dried.

The final isobutylene polymerization step was carried out by dissolving PSt-Br in a mixture of methylene chloride/hexane at -55°C, adding isobutylene, and ultimately the Et_2AlCl coinitiator. Since more aggressive conditions are necessary to achieve fast initiation of isobutylene from the tertiary bromine site than from the tertiary chlorine site, we used a stronger Lewis acid Et_2AlCl (than Et_3Al) and higher temperatures -55°C (rather than -70°C). Table 2 shows some representative examples of isobutylene polymerizations using PSt-Br and Et_2AlCl.

TABLE 2. Isobutylene Polymerizations Initiated by PSt-Br/Et_2AlCl[a,b]

Reaction conditions					Products[c]				
C_4H_8 (g)	PSt-Br (g)	Et_2AlCl ($\underline{M} \times 10^{-2}$)	Temperature (°C)	Time (min)	Conversion (%)	MEK insoluble (PSt-b-PIB, PIB)	MEK + pentane soluble (PSt-b-PIB)	MEK + heptane soluble (PSt-b-PIB)	Pentane or heptane insoluble (PSt)
2.1	0.92	1.4	-45	45	95	59% PSt content = 15%	38% PSt content = 66% $\overline{M}_n$ = 38,000	-	3% PSt content = 100%
31.5	7.8	1.4	-55	30	38	59% PSt content = 20%	27% PSt content = 70% $\overline{M}_n$ = 34,000	12% PSt content = 79% $\overline{M}_n$ = 35,000	2% PSt content = 100%
2.1	0.50	4.2	-65	30	43	16% PSt content = 17%	38% PSt content = 21% $\overline{M}_n$ = 42,000	44% PSt content = 47% $\overline{M}_n$ = 55,000	2% PSt content = 100%

[a] PSt-Br synthesis conditions: To a solution of styrene, 0.10 mole, in ethyl chloride, 80 ml, and Et_3Al, 4.8×10^{-3} mole, introduce 2-bromo-6-chloro-2,6-dimethylheptane, 8.0×10^{-4} mole, at -80°C; quench with methanol after 5 min; yield 7.7 g (74%), $\overline{M}_n$ = 20,000.

[b] Solvent for isobutylene polymerization, v/v: CH_2Cl_2/hexane = 65/25.

[c] Percent on basis of final polymer yield. Experimental error: Experiments 1 and 3 = 10%, Experiment 2 = 4%.

Concurrently with polymerization experiments, blank experiments were also run to monitor the purity of the reagents used. Thus monomer, solvent, and alkylaluminum coinitiator were combined in the same proportion as used for polymerization; however, no initiator was added. After quenching the polymerization and the blank experiments with methanol, the absence of any polymer in the blank was an indication of the satisfactory purity level of the chemicals used.

Since the possibility for chain transfer in isobutylene polymerization initiated by the PSt-Br/Et_2AlCl system exists, the possibility for homopolyisobutylene formation also arises. Consequently, a selective extraction procedure was developed to separate the pure poly(styrene-b-isobutylene) PSt-b-PIB from the crude product, i.e., that contaminated by homopolyisobutylene.

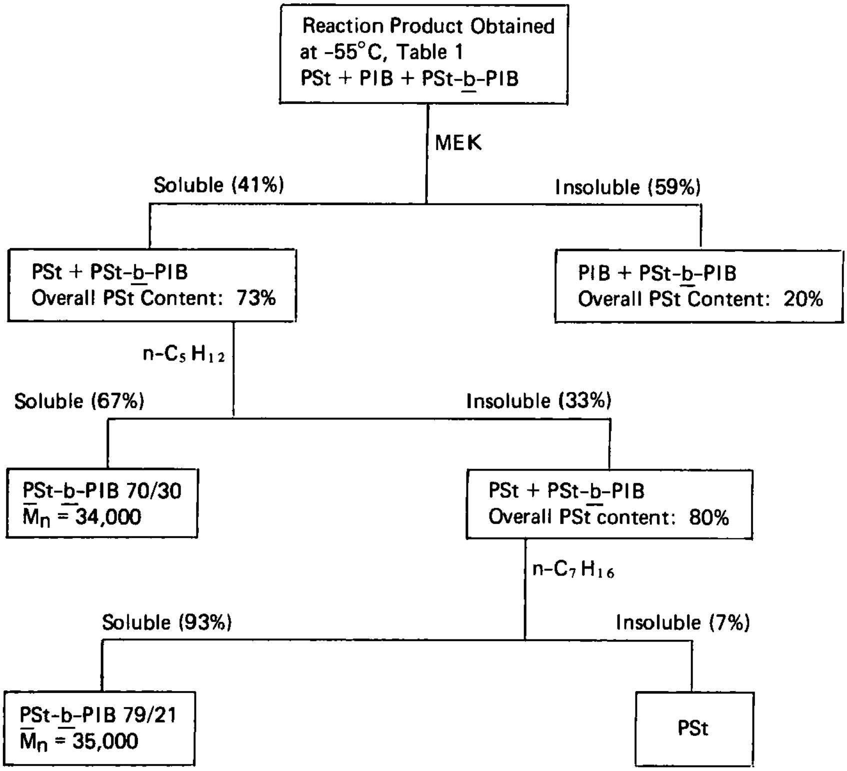
Scheme 1 illustrates our selective extraction procedure together with the yields (wt%) and composition (wt% by NMR) of the fractions obtained from the polymer prepared at -55°C. Methyl ethyl ketone, MEK, a nonsolvent for polyisobutylene, dissolves polystyrene and PSt-b-PIB, rich in polystyrene. The MEK-insoluble fraction contains homopolyisobutylene along with PSt-b-PIB of lower polystyrene content. The subsequent extraction of the MEK-soluble material with pentane and heptane, nonsolvents for polystyrene, resulted in soluble fractions containing pure PSt-b-PIB. The fact that only insignificant quantities (2 to 3%) of homopolystyrene were recovered demonstrates the substantial absence of chain transfer in the synthesis of PSt-Br and leads to the expected high levels of terminal t-bromine.

Since the higher molecular weight block copolymer was found to be insoluble in MEK, we were not successful in isolating homopolyisobutylenes and thus determine the total quantity of PSt-b-PIB formed. However, it can be seen from Table 2 that the MEK-insoluble fraction is smallest for the product obtained at -65°C, demonstrating the presence of a significantly lower amount of homopolyisobutylene. This is consistent with the fact that chain transfer is reduced at lower temperatures.

Gel permeation chromatography studies confirmed our extraction results.

Characterization

Solvent fractionation coupled with NMR, IR, and GPC studies established the existence of PSt-b-PIB. In addition to these



SCHEME 1. Extraction procedure used to obtain pure PSt-b-PIB.

analytical techniques, we have investigated the solubility and film behavior, glass transition temperature, and intrinsic viscosity of our block copolymer.

The PSt-b-PIB formed cloudy solutions in n-pentane (a solvent only for polyisobutylene) and in MEK (a good solvent only for polystyrene). In cyclohexane at room temperature slightly hazy solutions were obtained which, however, became clear when heated above the theta temperature of polystyrene (35°C), the temperature level beyond which cyclohexane becomes a good solvent for polystyrene. In contrast, the block copolymer formed visually clear solutions in toluene, benzene, and CCl_4, good solvents for both polystyrene and polyisobutylene.

Films cast from solutions of PSt-b-PIB in benzene were homogeneous and partially transparent. Films cast from cyclohexane were striped, presumably due to phase separations since cyclohexane is a poor solvent for polystyrene below 35°C.

The copolymer exhibited two T_g's (by DSC) at 369 and 199°K, characteristic of polystyrene and polyisobutylene, respectively.

The intrinsic viscosity, $[\eta]$, of PSt-b-PIB as a function of temperature in the range from 15 to 55°C is illustrated in Fig. 1. The viscosity increases rapidly to a maximum followed by a sudden decrease. After a minimum, $[\eta]$ again begins to increase. This abnormal temperature dependence of $[\eta]$ has been observed previously [9] and was shown to be characteristic of block and graft copolymers.

BIGRAFT COPOLYMERS: SYNTHESIS, CHARACTERIZATION, AND PHYSICAL PROPERTIES

Synthesis

It occurred to us that the principle of selective initiation, as described above in regard to the synthesis of PSt-b-PIB, could also be extended to the synthesis of bigraft copolymers. The basic plan was to select a suitable backbone polymer, chlorobrominate it to

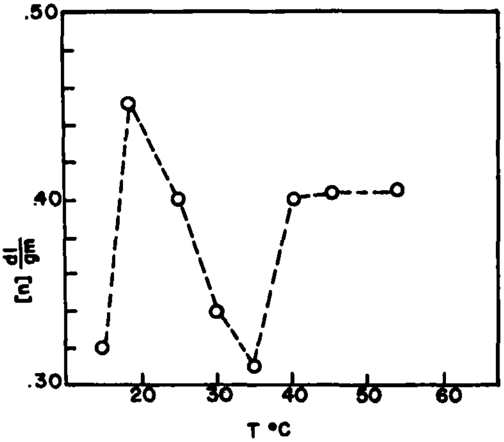


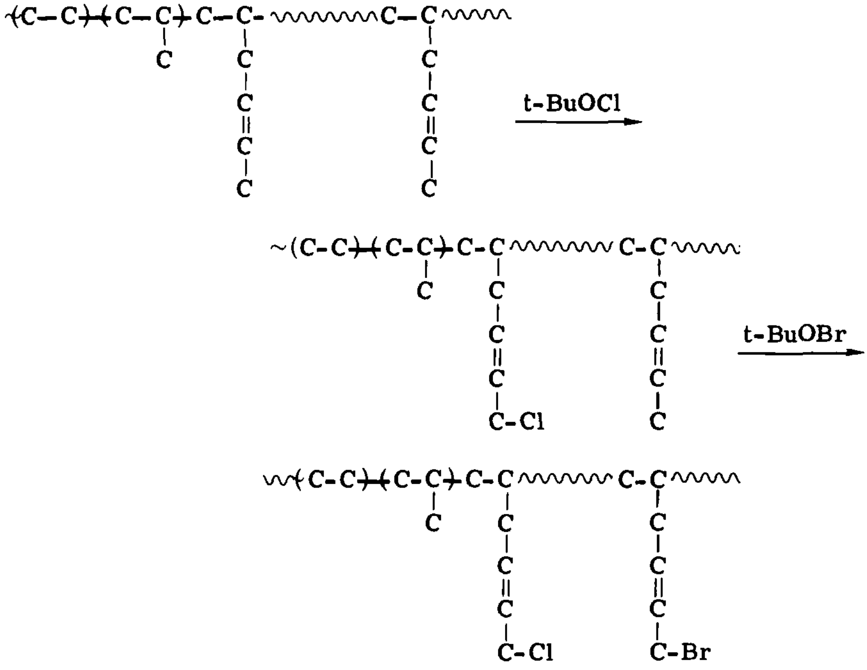
FIG. 1. The effect of temperature on the intrinsic viscosity of poly(styrene-b-isobutylene) in toluene.

produce a chain containing randomly distributed tertiary or allylic —Cl or —Br functions, and to use this species in conjunction with a suitable alkylaluminum compound for the selective sequential initiation of two monomers.

For a variety of reasons, such as ready availability, relatively simple microarchitecture, desirable solubility characteristics, and presence of tertiary and allylic positions, we decided to use Nordel-1440 for the backbone polymer. Nordel-1440 is a copolymer of ethylene and propylene containing a few percent 1,4-hexadiene. For the first monomer we chose styrene and for the second monomer α-methylstyrene or isobutylene.

The following scheme further illustrates the experimental procedure and provides some detailed information as to the chemicals used, copolymers contained, grafting efficiencies, molecular weights, etc:

1. The Backbone Polymer (Nordel):

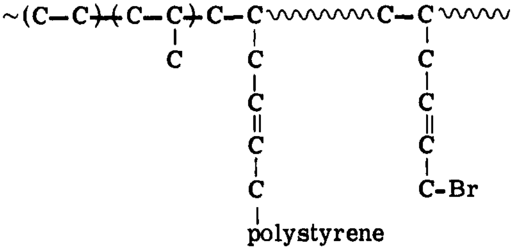


(ClBrNordel)

$\overline{M}_n$ = 57,000, Cl = 1.25%, Br = 5.88%.

2. The Monograft: Grafting of Styrene:

$$\text{ClBrNordel} \xrightarrow[\text{Et}_2\text{AlCl, -30°C}]{\text{styrene,}} \xrightarrow[\text{extractions}]{\text{acetone}}$$

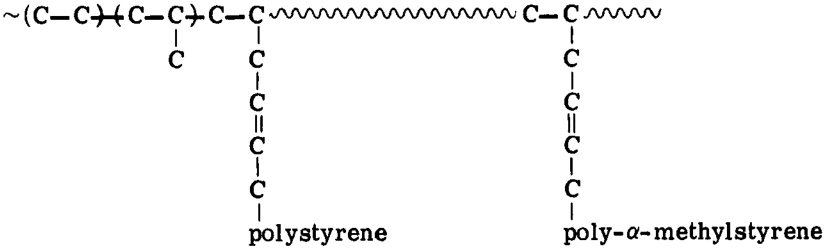


(BrNordel-g-polystyrene)

$\overline{M}_n$ = 98,000, G.E. = 40.5%, $\overline{M}_n$ homopolystyrene = 37,400.

3. The Bigraft: Grafting of α-Methylstyrene:

$$\text{BrNordel-g-polystyrene} \xrightarrow[\text{Et}_2\text{AlCl, -20°C}]{\alpha\text{-methylstyrene}} \xrightarrow[\text{extractions}]{\text{3-pentanone}}$$



(Nordel-g-polystyrene-g-poly-α-methylstyrene)

$\overline{M}_n$ = 189,000, G.E. = 11.7%.

Syntheses have also been performed in which the second monomer was isobutylene. This procedure yielded Nordel-g-polystyrene-g-polyisobutylene, $\overline{M}_n$ = 190,000.

A large amount of research effort was necessary to find suitable conditions for all the steps of these syntheses. For example, the allylic chlorobromination of Nordel had to be worked out. We preferred to use pendant allylic halogens as initiators because preliminary and other information indicated high allylic initiation activity coupled with selectivity. Also, the purification of first the monograft and subsequently the bigraft copolymers had to be worked out. We found acetone extractions to be satisfactory for the removal of the homopolystyrene formed via chain transfer in the first grafting step. Pertinent background information was available to guide us in accomplishing this purification step from previous work in this laboratory [10]. Thus a series of BrNordel-g-polystyrenes have been prepared and characterized. These materials are interesting thermoplastic elastomers whose properties are, obviously, quite similar to EPR-g-polystyrenes previously synthesized in our laboratories [10].

The purification of the bigrafts was a difficult undertaking. A large number of solubility and other studies was carried out before a satisfactory solution was found. A key finding was that cold 3-pentanone dissolves only homopoly-α-methylstyrene but not the Nordel-g-polystyrene-g-poly-α-methylstyrene bigraft. Interestingly, hot 3-pentanone can also be used to separate homopolyisobutylene in the Nordel-g-polystyrene-g-polyisobutylene synthesis. Whereas homopolyisobutylene is insoluble in boiling 3-pentanone, the bigraft dissolves in this solvent.

Another fractionation technique was to gel the bigraft (by treatment with sulfur monochloride) and extract all the soluble (i.e., nonbigraft) fraction.

The compositions of pure bigrafts were determined spectroscopically (IR, NMR); number-average molecular weights were established by osmometry and molecular weight distributions by GPC.

Table 3 shows some representative data.

Characterization and Physical Properties

At this time we wish to report some results in regard to our characterization and physical property studies carried out with various bigrafts.

The glass transition temperatures were determined by DSC. As expected, the Nordel-g-polystyrene-g-poly-α-methylstyrene and the Nordel-g-polystyrene-g-polyisobutylene both exhibited T_g's, indicating the presence of molecularly incompatible domains.

Stress-strain and permanent set data was obtained with microdumbbells prepared of solution cast films. Figure 2 shows some representative results.

TABLE 3. The Synthesis and Characterization of Bigraft Copolymers

Backbone (g) (initiator)	Monomer (M) Coinitiator (M) Solvents (v/v) T (°C)	Conversion (%)	Homopolymer[a]	Graft	Grafting efficiency (%)	Branches/ backbone
I. Nordel-g-PSt-g-PαMeSt						
	1. The Monograft Nordel-g-PSt					
ClBr-Nordel ~ 4 g $\overline{M}_n$ = 57,000	Styrene (1.5) $AlEt_2Cl$ (1.32 × 10^{-2}) n-Heptane/EtCl (85/15) -30	5.45	$\overline{M}_n$ = 37,400	Br-Nordel-g-PSt $\overline{M}_n$ = 98,000 PSt content = 17.6%	40.6	1.1
	2. The Bigraft Nordel-g-PSt-g-PαMeSt					
Br-Nordel-g-PSt ~ 4 g $\overline{M}_n$ = 98,000	α-Methylstyrene (1.5) $AlEt_2Cl$ (1.32 × 10^{-2}) n-Heptane/EtCl (80/20) -20	19	$\overline{M}_n$ = 51,500	Nordel-g-PSt-g-PαMeSt $\overline{M}_n$ = 189,000 PSt + PαMeSt content = 46.2%	11.7	1.8 (relative to PαMeSt grafts)

II. Nordel-g-PSt-g-PIB						
		1. The Monograft Nordel-g-PSt				
ClBr-Nordel ~ 4 g $\overline{M}_n$ = 57,000	Styrene (1.5) $AlEt_2Cl$ (1.32×10^{-2}) n-Heptane/EtCl (80/20) -30	16.6	$\overline{M}_n$ = 36,500	Br-Nordel-g-PSt $\overline{M}_n$ = 99,500 PSt content = 31.5%	30	1.16
		2. The Bigraft Nordel-g-PSt-g-PIB				
Br-Nordel-g-PSt ~ 4 g $\overline{M}_n$ = 99,500	Isobutylene (1.5) $AlEt_2Cl$ (1.32×10^{-2}) n-Heptane/EtCl (70/30) -30	44.05	$\overline{M}_n$ = 99,300	Nordel-g-PSt-g-PIB $\overline{M}_n$ = 190,000 PSt + PIB content = 64.05%	3.7	1.0 (relative to PIB grafts)

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[a] Molecular weights of extracted homopolymers.

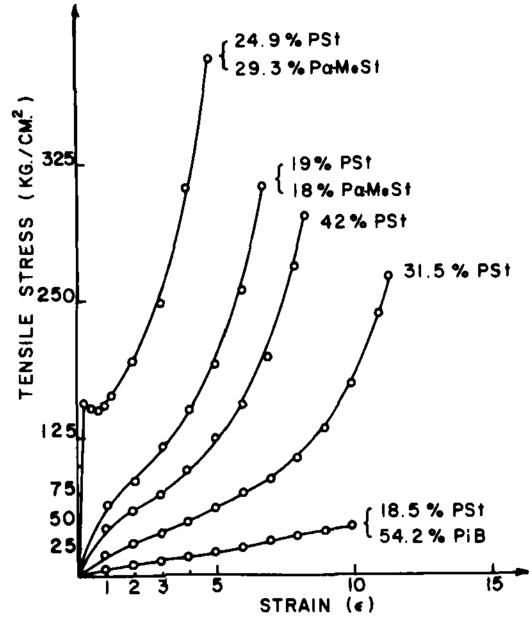

FIG. 2. Stress-strain properties of representative monograft and bigraft copolymers. The numbers indicate the composition of the branches of the graft.

ACKNOWLEDGMENTS

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REFERENCES

[1] J. P. Kennedy, Belgian Patent 663,319 (April 30, 1965).

[2] J. P. Kennedy and F. P. Baldwin, Belgian Patent 663,320 (April 30, 1965).

[3] J. P. Kennedy and S. Rengachary, Adv. Polym. Sci., **14**, 1 (1974).

[4] J. P. Kennedy, Makromol. Chem., **175**, 1101 (1974).

[5] M. Baccaredda, M. Bruzzone, S. Cesca, M. DiMaina, G. Ferraris, P. Giusti, P. L. Magagnini, and A. Priola, Chim. Ind., Milan, 55, 109 (1973).

[6] A. Priola, S. Cesca, and G. Ferraris, Makromol. Chem., 160, 41 (1972).

[7] J. P. Kennedy, J. J. Charles, and D. L. Davidson, in Recent Advances in Polymer Blends, Grafts and Blocks (L. H. Sperling, ed.), Plenum, New York, 1974, p. 157.

[8] J. P. Kennedy, N. V. Desai, and S. Sivaram, J. Amer. Chem. Soc., 95, 6386 (1973).

[9] A. Dondos, Makromol. Chem., 99, 275 (1966).

[10] J. P. Kennedy and R. R. Smith, in Recent Advances in Polymer Blends, Grafts and Blocks (L. H. Sperling, ed.), Plenum, New York, 1974, p. 303.