VINYL POLYMERIZATION

V. Synthesis of Graft Polymers from Brominated Poly (Styrene)

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ABSTRACT

Vinyl monomer [methyl methacrylate (MMA), or ethyl methacrylate (EMA) or methyl acrylate (MA)] was polymerized in benzene solution with benzoyl peroxide as catalyst and in the presence of varying amounts of bromopoly (styrene) (Br PS). Branching occurred by chain transfer reaction of the growing polymer radicals with bromine atoms of the biomopoly (styrene) backbone, followed by initiation of polymerization by the Br PS radicals thus obtained. The chain transfer constants of the branching reaction and the degree of grafting were determined and by suitable correlation of the two, $k_g/(k_t)^{\frac{1}{2}}$ for the grafting reactions were evaluated. The graft polymers were isolated by fractional precipitation, and were characterized by IR spectra and molecular weight determination by osmotic pressure measurements. The high values of chain transfer constant, molecular weight of the graft polymers much in excess of the backbone Br PS, the order of magnitudes of second virial coefficients, etc., proved the formation of graft polymers.

I. INTRODUCTION

THE role of bromine atoms as reactive sites for chain transfer in vinyl polymerization is well known.[1] Schonfeld and Waltcher[2] synthesized a graft polymer consisting of branches of poly (styrene) over a backbone of a polyester of pentaerythritol dibromide and adipic acid. Saigusa and Oda[3] described the synthesis of brompoly (styrene) and obtained a graft polymer containing branches of poly (vinyl acetate) after partial dehydrobromination of Br Ps, but no detailed study of the grafting reactions or characterization of graft polymers was made. We report in this paper, synthesis, isolation and characterization of graft polymers with bromopoly (styrene) (Br PS) as backbone and side chains of poly (methyl methacrylate), PMMA; poly (ethyl methacrylate), PEMA and poly (methyl acrylate), PMA respectively. These graft polymers are designated as: Br PS-g-PMMA, Br PS-g-PEMA, and Br PS-g-PMA respectively.

II. EXPERIMENTAL

(a) *Reagents and chemicals.*—The monomers MMA, EMA and MA (Rohm and Haas Co., U.S.A.) were purified from inhibitors by washing with sodium hydroxide (10%) solution and distilled twice under reduced nitrogen-pressure (10–15 mm.), the middle cuts being used for polymerization experiments. The solvents benzene, carbon tetrachloride, methyl ethyl ketone (MEK), petroleum ether (*n*-hexane, b.p. 60–80° C.), methanol, etc., were purified by standard procedures and distilled before use. Benzoyl peroxide (Riedel-de Haen Ag, Germany) was purified by recrystallization from 1 : 1 mixture of cold chloroform and methanol. N-bromosuccinimide (BDH England) was used as such without purification.

(b) *Preparation[3] of bromopoly (styrene).*—Poly (styrene) (22·5 gm.) was dissolved in carbon tetrachloride (300 gm.) in a three-necked flask provided with a mercury-seal stirrer and a reflux condenser. N-bromosuccinimide (44 gm.) and moistened benzoyl peroxide (11·0 gm.) were then added, the contents of the flask were stirred vigorously and refluxed for 220 mins. The contents were then cooled, filtered to remove succinimide and the filtrate was poured into methanol (500 ml.) with stirring. The precipitate of bromopoly (styrene) (with Br both on aliphatic and aromatic carbon atoms[3]) was collected, purified by reprecipitation from benzene/methanol mixtures, and dried in vacuum at about 40° C. The bromine content of Br PS thus prepared was found to be 17% by weight by microanalysis.

(c) *Polymerization procedure.*—An ampoule (25 ml. capacity with 3″ long stem) was charged with calculated quantities of Br PS (0–0·4 m./l.), monomer (1·5 m./l.) and benzoyl peroxide catalyst (5 × 10⁻³ m./l.) and solvent in required amounts was added to make up the volume of the mixture to about 12 ml. Oxygen-free nitrogen was passed through the cooled solution in the ampoule for 15 minutes, the narrow stem of the latter was then sealed and placed in a constant temperature bath at 70° C. ± 0·1° C. (maintained by a regulator and a relay) for 3 hours. The ampoule was then removed, cooled in ice, the stem broken and the contents emptied into excess of petroleum ether when the polymer (unreacted Br PS, graft polymer and newly formed homopolymer) precipitated. The polymer was dried to constant weight.

(d) *Fractionation and isolation of graft polymers.*—The products after the grafting reaction consisted of the following: unreacted Br PS, graft polymer and homopolymer (PMMA, or PEMA or PMA). For the separation of these mixtures, fractional precipitation procedure similar to that

adopted by Smets[4] was empolyed. It was found that in methyl ethyl ketone-methanol mixtures the backbone, graft- and homopolymers had sufficiently different solubility characteristics so as to enable separation at successive stages by precipitation and centrifugation. Preliminary experiments were conducted with Br PS, PMMA, PEMA or PMA to find out the volume fraction (γ-value) of methanol required for commencement of precipitation from a 2% solution of the polymer in MEK. The results of the precipitation titrations were plotted in terms of percentage of polymer precipitated (V_s) volume fraction (γ-value) of methanol. The precipitation titrations were also conducted for mixtures of polymers: Br PS + PMMA or PEMA (3:7) since under the experimental condition, the ratio of Br PS; PMMA, etc., was found to be 3:7. The precipitation titrations are shown in Fig. 1. The precipitation ranges (in terms of γ-values of methanol) for the polymers were: Br PS: $\gamma = 0\cdot10-0\cdot35$; PMMA: $\gamma > 0\cdot55$; PMA: $\gamma > 0\cdot65$; PEMA: No precipitation; Br PS-g-PEMA: $\gamma = 0\cdot80-0\cdot83$;
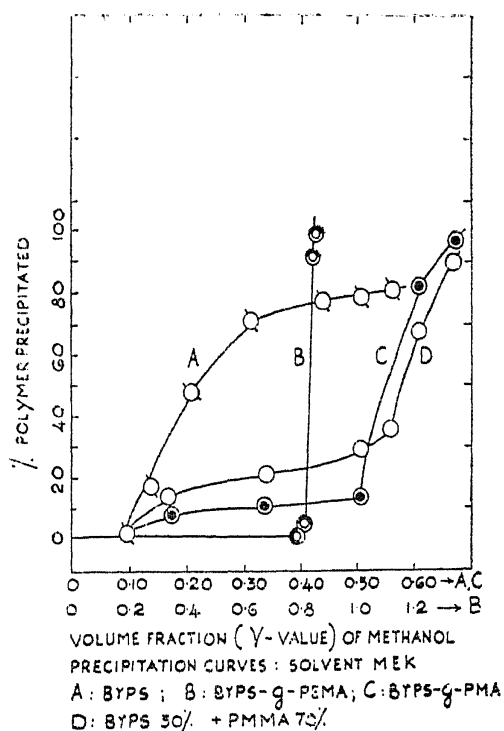

FIG. 1. Precipitation curves: Solvent Mek A: BrPS; B: BrPS-g-PEMA; C: BrPS-g-PMA D: BrPS 30% + PMMA 70%.

Br PS-g-PMA: $\gamma = 0\cdot50-0\cdot65$, etc. The graft and homopolymers were thus separated by centrifugation in the corresponding range of γ-values. The graft polymers were purified by repeated dissolution in methyl ethyl ketone and precipitation by addition of methanol.

(e) (i) Measurement of the degree of polymerization P_n and (ii) evaluation of chain transfer constant C_p.

The degrees of polymerization of the homopolymers (PMMA or PEMA or PMA) were determined by measurement of intrinsic viscosity of the polymer solutions making use of an Ubbelhode type suspended level dilution viscometer. The following relationships were used for computing the chain lengths from intrinsic viscosity:—

For the system PMMA/benzene[5] at 30° C.,

$$P_n = 2 \cdot 22 \times 10^3 \, [\eta]^{1 \cdot 32}.$$

For the system PEMA/methyl ethyl ketone[6] at 25° C.

$$[\eta] = 1 \cdot 44 \times 10^{-5} \, \bar{M}_n^{0 \cdot 88}$$

and for the system PMA/acetone[7] at 20° C.

$$P_n = 11 \cdot 2 \, [\eta]^{1 \cdot 22}, \quad [\eta] \text{ in ml. g}^{-1}$$

where $[\eta]$, P_n and $\bar{M}_n$ refer to the intrinsic visocosity, degree of polymerization and number-average molecular weight respectively.

(ii) The chain transfer constant (growing polymer radical and backbone) C_p was evaluated from the equation[8, 9]

$$\frac{1}{P_n} - \frac{1}{P_{no}} = C_p \frac{[P]}{[M]}$$

where [P] and [M] refer to the concentration of the backbone polymer (in terms of moles of structural unit) and monomer respectively, P_n and P_{no} the degrees of polymerization of the homopolymer in the presence and absence of the backbone polymer respectively, $C_p = k_3/k_4$ (ref. discussion below). From the plots of

$$\frac{1}{P_n} - \frac{1}{P_{no}} (V_s) \frac{[P]}{[M]}$$

C_p was evaluated (Fig. 2, Table II).

(f) *Grafting efficiency* (GE) *and rate of polymerization.*—Grafting efficiency was computed gravimetrically from the weight of unbound homopolymer and total weight of homopolymer (unbound and bound).

$$GE = \frac{\text{Weight of bound homopolymer as grafts}}{\left\{ \begin{array}{c} \text{weight of unbound homopolymer} \\ + \text{weight of the bound homopolymer as grafts} \end{array} \right\}} \, .$$

The grafting efficiencies for various reactions varied from 0·1 to 0·5 (Table I). The rate of homopolymerization (R_h) and rate of total polymerization (homo + graft) (R_p) were determined from the weights of the corresponding polymers obtained in graft polymerization experiments. The rate of graft polymerization R_g was obtained from the difference:
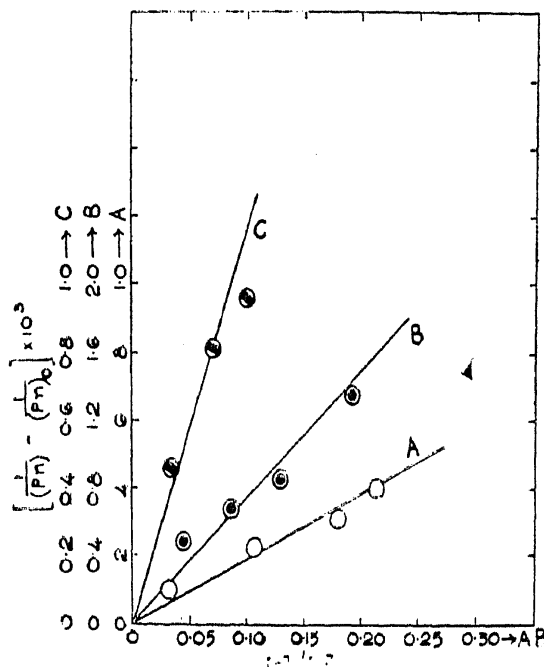
$$R_g = R_p - R_h$$

FIG. 2. A: [BrPS]/[MMA]; B: [BrPS]/[EMA]; C: [BrPS]/[MA].

and

$$GE = \frac{R_g}{R_p} .$$

(g) *Osmotic pressure measurements.*—A Pinner-Stabin[10,11] osmometer (Polymer Consultants Ltd., England, Colchester) was used with PECL 600 Gel Cellophane membranes previously conditioned in the solvent to be used for osmotic pressure measurements. Polymer solutions of concentration < 0·6 gm./100 gm. were used. Osmotic pressure head was measured by a static method after more than 15 hours equilibration at 30° C. The results were treated according to the equation[12,13]

$$\left(\frac{\pi}{C}\right)^{\frac{1}{2}} = \left(\frac{\pi}{C}\right)_0^{\frac{1}{2}} [1 + \tfrac{1}{2}T_2c]$$

where π is osmotic pressure, $(\pi/c)_0 = RT/\bar{M}_n$ and the second virial coefficient $A_2 = T_2/\bar{M}_n$. $\bar{M}_n$ and A_2 were calculated from the intercepts and slopes of

Table I

Synthesis of graft polymers

Graft polymer	(P) moles lit.$^{-1}$	Grafting efficiency
1. Br PS-g-PMMA		
[Monomer] = 1·47 moles lit.$^{-1}$ ..	0·320	0·16
[Bz$_2$O$_2$] = 5·00 × 10^{-3} moles lit.$^{-1}$ ..	0·267	0·13
Solvent: benzene. Temperature: 70 °C.	0·157	0·04
2. Br PS-g-PEMA—		
[Monomer] = 1·25 moles lit.$^{-1}$ ..	0·159	0·22
[Bz$_2$O$_2$] = 5·15 × 10^{-3} moles lit.$^{-1}$ ..	0·106	0·21
Solvent: benzene, Temperature: 70° C. ..	0·053	0·15
3. Br PS-g-PMA		
[Monomer] = 1·62 moles lit.$^{-1}$ ..	0·159	0·48
[Bz$_2$O$_2$] = 62·5 × 10^{-3} moles lit.$^{-1}$ ..	0·106	0·42
Solvent: benzene, Temperature: 70° C. ..	0·053	0·33

the plots $(\pi/c)^{\frac{1}{2}}$ (*vs.*) c (Fig. 3). The polymer-solvent interaction parameter $\psi(1 - \Theta/T)$ was calculated from

$$A_2 = \frac{\bar{v}^2}{V_1} \psi (1 - \Theta/T) FX$$

where $\bar{v}$, the partial specific volume of the polymer (assumed to be unity), V_1 the molar volume of the solvent and $F(X)$ a function of the degree of expansion of the coiled polymer molecules. The value $F(X)$ was assumed to be unity for our systems. The results are presented (Table IV).

III. Results and Discussion

(a) Mechanism of Grafting Reaction

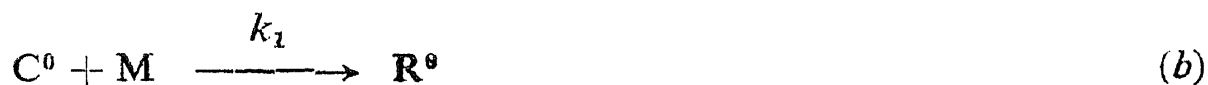The following sequence of reactions leading to the formation of graft and homopolymers are considered important,

(i) Production of radicals:

$$\text{Catalyst} \xrightarrow{k_d f} 2\,C^0 \tag{a}$$

(benzoyl peroxide)

(ii) Initiation:

(1) homopolymer

$$C^0 + M \xrightarrow{k_1} R^0 \tag{b}$$

(2) graft polymer
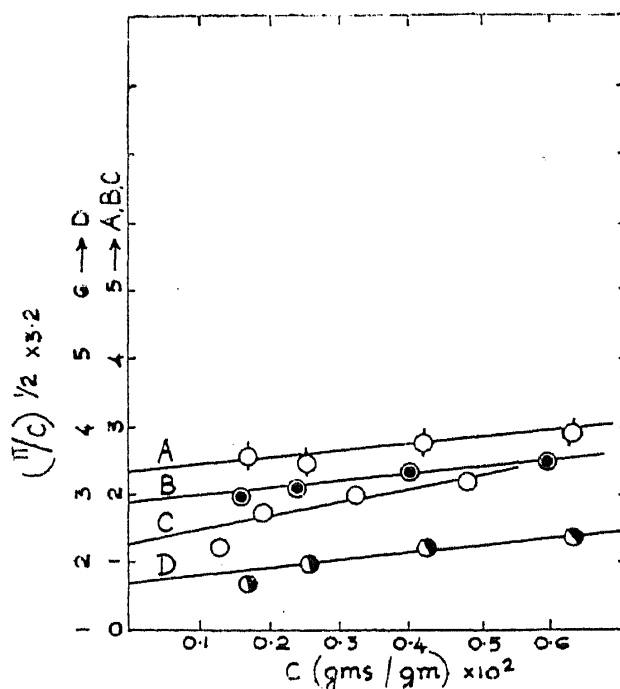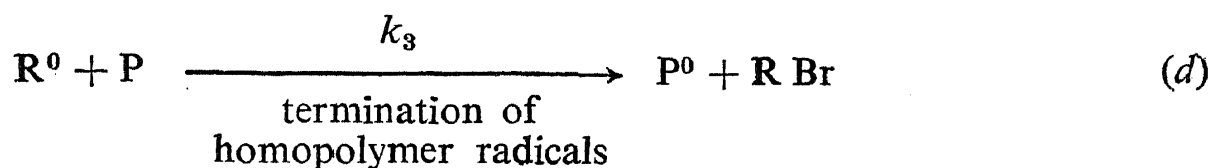
$$C^0 + P \xrightarrow{k_2} P^0 \text{ (insignificant)} \tag{c}$$

FIG. 3. A: BrPS/MEK; B: BrPS-g-PMA/MEK; C: BrPS-g-PMMA/MEK; D: BrPS-g-PEMA/MEK.

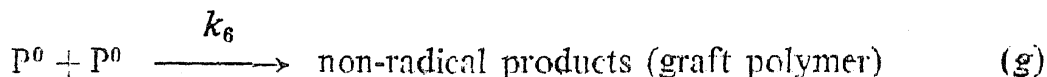chain transfer and production of backbone radicals;

$$R^0 + P \xrightarrow[\text{termination of}]{k_3} P^0 + R\,Br \tag{d}$$

homopolymer radicals

(iii) Propagation:

(1) Homopolymer:

$$R^0 + M \xrightarrow{k_4} R^0 \tag{e}$$

(2) graft polymer

$$P^0 + M \xrightarrow{k_5} P^0 \qquad\qquad (f)$$

(iv) Termination:

(1) Graft + graft:

$$P^0 + P^0 \xrightarrow{k_6} \text{non-radical products (graft polymer)} \qquad (g)$$

(2) graft and homo:

$$P^0 + R^0 \xrightarrow{k_7} \text{non-radical products (graft + homo)} \qquad (h)$$

(3) homo + homo

$$R^0 + R^0 \xrightarrow{k_8} \text{homopolymer} \qquad\qquad (i)$$
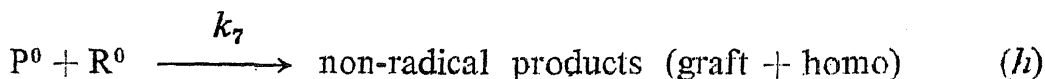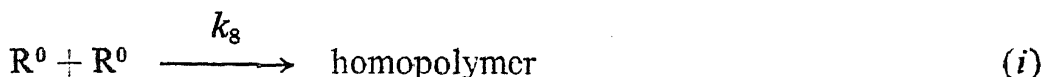
where C^0 = catalyst radical, R^0 = homopolymer radical, P = backbone molecule, P^0 = backbone radical or graft polymer radical (both the reactivities being assumed to be the same; k_d = decomposition rate constant of benzoyl peroxide, f = initiator efficiency. Applying stationary state principle to the above sequence of reactions, the following expression was obtained[9]:

$$\frac{GE}{C_p} \cdot \frac{R_p}{R_h} = \frac{k_5}{(k_6)^{\frac{1}{2}}} \frac{[P]}{(2k_d f\,[\text{cat}])^{\frac{1}{2}}} + \frac{k_5}{k_3} \cdot \frac{k_7}{k_6}$$

where GE = grafting efficiency, $C_p = k_3/k_4$ (chain transfer constant); R_p = total rate of polymerization; R_h = rate of homopolymerization, $[P]$ = backbone concentration, etc., plots of $(GE/C_p)\,(R_p/R_h)\,(V_s)\,[P]$ are shown (Fig. 4). From the slopes of the plots, the ratio $k_5/(k_6)^{\frac{1}{2}}$ was obtained. The values $k_d = 1\cdot41\times10^{-4}$ sec.$^{-1}$ and $f = 0\cdot72$ were used.[14,15] The values of $k_5/(k_6)^{\frac{1}{2}}$ (analogous to $k_p/(k_t)^{\frac{1}{2}}$) for grafting reactions were calculated (Table II) and compared with $k_p/(k_t)^{\frac{1}{2}}$ for the homopolymerization of MMA, EMA and MA calculated from available data of Matheson *et al.*[16] Although $k_5/(k_6)^{\frac{1}{2}}$ values for the grafting reaction were lower than $k_p/(k_t)^{\frac{1}{2}}$ values for homopolymerization reaction, the agreement may be considered to be satisfactory in view of the specific nature of the grafting reaction, specific configurational effects of the polymer radicals and mutual compatibility of the backbone and side chains coming into play.

(*b*) *Application of Chain Transfer Data to Q — e Scheme*

It was suggested by Voeks[17] that chain transfer data for polymer-polymer transfer reactions may be correlated on the basis of the following semi-empirical expression:

$$C_p = \frac{Q_p}{Q_M} \exp. e_M [(e_M - e_p)]$$

where C_p is the transfer constant (polymer radical + poolymer backone). Q_p and Q_M are the ' Q ' values (specific reactivity), e_p and e_M the ' e ' values (polarity) for the backbone polymer and grafting monomer respectively.

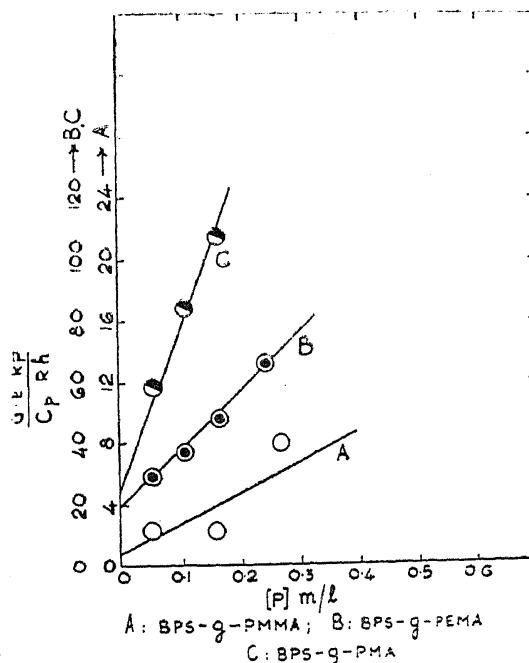A: BPS-g-PMMA; B: BPS-g-PEMA
C: BPS-g-PMA

FIG. 4. A: BPS-g-PMMA; B: BPS-g-PEMA; C: BPS-g-PMA.

Making use of the values of Q_M and e_M for MMA, EMA and MA from copolymerization data[18] and experimentally determined C_p values by us for the grafting reactions, the Q_p and e_p values for the backbone Br PS were computed and compared with ' Q ' and ' e ' values for hydrocarbon solvents tabulated by Voeks[17] and Katagiri *et al.*[19] It is interesting to observe that the Q_p and e_p values for the polymer Br PS are higher than Q and e values for hydrocarbon solvents like C Br_4, etc., indicating a greater reactivity and higher polarity for polymeric radicals. Excellent agreement is found between the Q_p and e_p values calculated from the C_p data for different pairs of backbone-monomer combinations. Thus the Q — e scheme for polymer-polymer transfer reactions appears to be of general applicability in the sense that when once Q_p

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Table II

Chain transfer constants and $(k_5/k_6)^{\frac{1}{2}}$ values (70° C.)

Polymer (P)	Monomer (M) (side chain)	$C_p = k_3/k_1 \times 10^3$	$k_5/(k_6)$ for grafting reaction	$k_5/(k_4)$ for homopoly-merization
Br PS	MMA	18·4	0·07	0·112 (60° C.)
Br PS	EMA	6·20	0·19	—
Br PS	MA	8·50	0·61	0·964 (60° C.)

and e_p values for a particular polymer are obtained, then C_p for any grafting (branching) reaction may be calculated making use of the values of Q_M and e_M for the grafting monomer from the literature. The Q_p and e_p values for Br PS are listed in Table III.

Table III

Q — e values for Br PS

Polymer		$Q_p \times 10^3$	e_p
Br PS	..	249·7	+7·66
Br PS	...	381·7	+8·72
Br PS (solvent)	..	351·10	+8·23
C Br₄	..	310·0	+1·63
Trichlorobromomethane	..	38·9	+3·90

Calculated from $C_p = Q_p/Q_M$ exp. $[e_M(e_M - e_p)]$.

(c) Characterization of Graft Copolymers

(i) *Infra-red spectra.*—The IR spectra of the graft polymers showed absorption at $\lambda = 6·28$–$6·30\,\mu$ characteristic of phenyl group (present in Br PS but not in the side chain) and absorption at $\lambda = 5·8\,\mu$ characteristic of C = O group (present in PMMA, PMA or PEMA but not in Br PS).

Thus the presence of backbone and side chain was revealed by IR spectra. Typical IR spectrum is shown (Fig. 5).
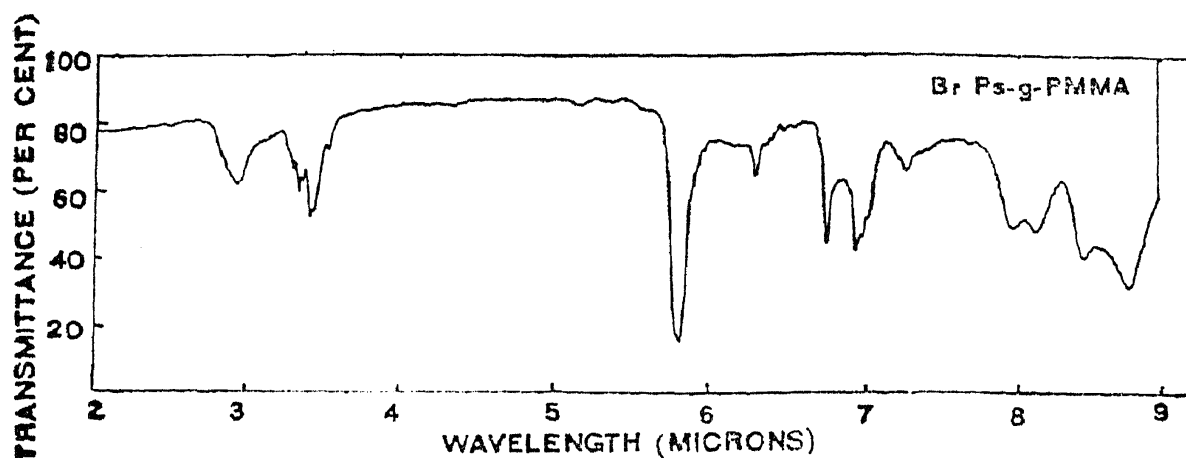

FIG. 5. Infra-red spectrum of a typical graft polymer (Br PS-g-PMMA).

(ii) *Molecular weight determination.*—It is an obvious fact that a better method of characterization of a graft polymer is by comparison of its molecular weight with that of the backbone. For instance, in the IR spectrum, absorption bands of characteristic groups of both the polymers (backbone and side chain polymer) will be observed whether they are chemically bound as in graft polymer or not bound as in mechanical mixtures of the constituent polymers. But chemical binding between two polymers (*e.g.*, Br PS with

TABLE IV

Molecular weight data (osmotic pressure measurements) in methyl ethyl ketone, 29° C.

Polymer		M_n $\times 10^{-5}$	T_2 $\times 10^{-2}$	Λ_2 $\times 10^4$	$\psi(1-\Theta/T)$ $\times 10^2$	% of side chain
Br PS	..	0·465	1·54	33·0	29·61	..
Br PS-g-PMMA	..	1·52	2·042	17·39	15·57	60·42
Br PS-g-PEMA	..	0·888	1·176	13·23	11·85	47·66
Br PS-g-PMA	..	0·711	1·052	14·78	13·23	34·62
PMMA (*)	..	..	..	1·66	..	..
PEMA(*)	..	..	..	1·83	..	..

(*a*) Calculated from S. N. Chinai *et al.*[29]

(*b*) Calculated from S. N. Chinai *et al.*[21]

PMMA, or PEMA or PMA) can be directly proved by molecular weight determination. The graft polymers had increased molecular weight in excess of the backbone (Br PS) thus indicating the presence of graft side chains (Table IV). From the increase in molecular weight as a result of grafting, the percentage of side chain polymer in the graft polymer was calculated. The second virial coefficient A_2 and the polymer-solvent interaction parameters ψ $(1 - \Theta/T)$ (Table IV) for the graft polymers were intermediate between the corresponding values for Br PS and PMMA, PEMA or PMA providing additional evidence for graft polymer formation.

ACKNOWLEDGEMENT

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