

Graft Polymerization of Isobornyl Acrylate and Isobornyl Methacrylate onto *cis*-Polybutadiene - A Kinetic Study

T. SRILATHA and P. RAGHUNATH RAO*

Department of Chemistry, Kakatiya University, Warangal-506 009, India

E-mail: raghunath_pemma@yahoo.com

The radical induced grafting of isobornyl acrylate (IBA) and isobornyl methacrylate (IBM) onto *cis*-polybutadiene (PBD) has been studied in toluene at 70°C using benzoyl peroxide (BPO) as an initiator. The effect of monomer concentration on grafting yield shows that the grafting yield increases up to 0.60 monomer concentration and then remains almost constant. A logarithmic plot of rate of grafting against monomer concentration gives a linear relationship giving order with respect to IBA as 1.33 and IBM as 1.22. The formation of graft copolymers and the site of grafting were confirmed by IR spectra. The grafting of IBA on PBD occurred on the double bond position and that of IBM on vinylic position. The grafting yield was increased with increasing initiator concentration up to 0.030 g. The variation of graft yield with reaction time shows that grafting yield increased initially with increase in the reaction time and then remained almost constant. Increasing temperature increases the graft yield up to certain temperature and then it decreases at higher temperature. This is due to the mutual termination of initiating free radicals. Thermogravimetric analysis has been studied for homo- and graft copolymers. Initial decomposition temperature (IDT) and decomposition temperature at 50 % weight loss have been determined. Intrinsic viscosity measurements on the graft copolymer has been determined.

Key Words: Graft copolymers, Isobornyl acrylate, Isobornyl methacrylate, *cis*-Polybutadiene.

INTRODUCTION

Nai-Jan and Sundberg¹ studied the grafting of styrene, acrylate and methacrylate monomers onto *cis*-polybutadiene (*cis*-PBD) using azo-bis-isobutyronitrile (AIBN) as initiator in solution polymerization. Cameron *et al.*² has studied the radical grafting of methyl methacrylate onto PBD in benzene solution at 60°C using benzoyl peroxide (BPO) as initiator. Ling Yum *et al.*³ studied the graft copolymerization of styrene- maleic-anhydride and *cis*-PBD. Chandra Siri *et al.*⁴ studied the graft copolymerization of acrylic acid onto acrylonitrile-butadiene-terpolymer using BPO as

initiator. They observed that addition occurs in the butadiene region of the polymer, either by the loss of vinylic hydrogen and subsequent radical formation or by the addition to the double bond. The graft copolymers were characterized by IR and TGA. On the basis of IR spectra they concluded that the grafting occurs at the double bond position of the butadiene. In our earlier papers we have discussed the formation of random copolymers using acrylonitrile (AN)⁵, methacrylonitrile (MAN)⁶, N-methyl acrylamide (NMA)⁷ and N,N-dimethyl acrylamide (NNMA)⁸ with isobornyl acrylate (IBA) and isobornyl methacrylate (IBM) using AIBN as initiator. Reactivity ratios, microstructure of copolymers, solution, thermal and dielectric properties of these copolymers were discussed. The present paper deals with the optimum conditions required for grafting of IBA/IBM onto *cis*-PBD, the effect of concentration of monomer, initiator, temperature, reaction times and the site of grafting onto PBD using IR studies, thermal and viscosity measurements on graft copolymer have been discussed.

EXPERIMENTAL

The monomers IBA (Aldrich) and IBM (Lancaster) were purified⁷ before use. *cis*-PBD (Aldrich) was purified before use. BPO (Fluka) was recrystallized before use. The solvent used in the copolymerization was toluene which is a reagent grade chemical and was distilled before use.

Synthesis of homo- and copolymers

All experiments were performed in glass tubes with appropriate quantities of dry monomers, solvent and initiator⁷. The tubes were then sealed in an atmosphere of nitrogen and then were introduced into the thermostat at 70°C temperature. Polymerizations were carried out in toluene solvent in the presence of BPO. After a given time, the polymerization mixture was poured into a large amount of water to isolate the polymer, which was filtered and washed thoroughly with water followed by ether and hexane for purification. Then it was dried under vacuum:

Calculation of percentage of grafting (G): The percentage of grafting (G) was determined gravimetrically by using the following relation⁹:

$$\% \text{ Grafting (GP)} = (A-B)/B \times 100 \quad (1)$$

where A = the weight of grafted PBD, B = the weight of original PBD after complete removal of the unreacted monomer.

$$\text{Grafting efficiency (GE) (\%)} = (A-B)/C \times 100 \quad (2)$$

C = the weight of the monomer.

The rate of grafting (Rg) was calculated by the method reported by Kumar *et al.*¹⁰:

$$R_g \text{ (molL}^{-1} \text{ s}^{-1}\text{)} = \frac{\text{Weight grafted monomer} \times 100}{\text{m.w. of monomer} \times \text{Time of polymerization} \times \text{Volume of reaction mixture}} \quad (3)$$

RESULTS AND DISCUSSION

The radical induced grafting of IBA and IBM onto *cis*-PBD has been studied in toluene at 70°C using BPO as initiator.

Effect of monomer concentration: The effect of monomer concentration on the grafting yield was studied by keeping the weight of PBD and the initiator constant at 0.500 and 0.050 g, respectively. All the reactions were performed for 2 h in 100 mL reaction mixture at 70°C. In each experiment the concentration of monomer (IBA/IBM) was changed and the results are given in Table-1. The graft yield increased initially with increase in monomer concentration up to 0.600 and then remained almost constant for both monomers. This may be because initially the number of monomer molecules diffusing through the reaction and reaching the free radical sites on the PBD backbone govern the grafting extent. Whereas at higher concentrations of monomer, the graft yield remains almost constant as the number of the radical sites available on the PBD backbone becomes a limiting factor. This was also supported by the results obtained on the rate of grafting (Table-1). Similar results were observed on the grafting reaction onto polypropylene¹¹. The order of reaction was determined with respect to monomer¹² concentration by plotting the logarithm plots of rate of grafting vs. concentration of IBA/IBM. This gives a linear relationship with order of 1.33 for IBA and 1.22 for IBM.

TABLE-1
EFFECT OF CONCENTRATION OF MONOMER ON GRAFTING ONTO
CIS-POLYBUTADIENE

IBA (g)	Effect of IBA ^a			IBM (g)	Effect of IBM ^a		
	Graft yield (%)	Graft efficiency (%)	Rg (mol L ⁻¹ s ⁻¹)		Graft yield (%)	Graft efficiency (%)	Rg (mol L ⁻¹ s ⁻¹)
0.075	17	113.33	1.47×10^{-5}	0.075	16	106.66	1.30×10^{-5}
1.500	24	80.00	3.69×10^{-5}	1.500	22	73.33	3.17×10^{-5}
0.300	58	96.66	14.50×10^{-5}	0.300	51	85.00	11.94×10^{-5}
0.600	93	77.50	33.82×10^{-5}	0.600	87	72.50	29.64×10^{-5}
0.900	94	52.22	40.29×10^{-5}	0.900	89	49.44	35.74×10^{-5}
1.200	96	40.00	45.18×10^{-5}	1.200	90	37.50	39.68×10^{-5}

^a0.500 g PBD, 0.050 g BPO, 2 h in 100 mL at 70°C.

Effect of initiator concentration: The effect of initiator concentration on the graft yield was studied by keeping the weight of the PBD and the monomer IBA/IBM constant at 0.500 and 0.600 g, respectively and changing the initiator concentration. The results are shown in Table-2. The graft yield increased initially with increase in the initiator concentration and it was almost same for any amount of BPO above 0.030 g. This also

supported by the results obtained for the rate of grafting (Rg) (Table-2). Similar observations were reported for grafting of acrylic acid⁴ onto PBD and styrene onto PBD^{13,14}.

TABLE-2
EFFECT OF CONCENTRATION OF INITIATOR ON GRAFTING OF IBA
AND IBM ONTO CIS-POLYBUTADIENE

BPO (g)	IBA ^a grafting			BPO (g)	IBM ^b grafting		
	Graft yield (%)	Graft efficiency (%)	Rg (mol L ⁻¹ s ⁻¹)		Graft yield (%)	Graft efficiency (%)	Rg (mol L ⁻¹ s ⁻¹)
0.010	53	44.16	16.06 × 10 ⁻⁵	0.010	49	40.83	13.91 × 10 ⁻⁵
0.020	74	61.66	22.42 × 10 ⁻⁵	0.020	78	65.00	22.15 × 10 ⁻⁵
0.030	95	79.16	28.79 × 10 ⁻⁵	0.030	86	71.66	24.42 × 10 ⁻⁵
0.040	96	80.00	29.09 × 10 ⁻⁵	0.040	84	70.00	23.85 × 10 ⁻⁵
0.050	93	77.50	28.18 × 10 ⁻⁵	0.050	87	72.50	24.70 × 10 ⁻⁵
0.060	91	75.83	27.58 × 10 ⁻⁵	0.060	82	68.33	23.28 × 10 ⁻⁵

^a0.500 g PBD, 0.600 g IBA, 2 h in 100 mL at 70°C.

^b0.500 g PBD, 0.600 g IBM, 2 h in 100 mL at 70°C.

Effect of reaction time: The effect of reaction time on graft field was studied by keeping the weight of PBD, monomer (IBA/IBM) and the initiator constant at 0.500, 0.600 and 0.030 g, respectively. For each reaction the reaction time has been changed and the results are tabulated in Table-3. The graft yield increased initially with increase in the reaction time and then remained constant with further increase in time. The radicals had more time for participating in the reaction, and as a result, will increase in per cent of grafting was noted. After sometime, all the initiator was used up. As a result, no further change in grafting percentages was observed with an increase in reaction time. The reaction time for the two monomers was different and this result was supported by the results of rate of grafting (Table-3). The same type of results were obtained for grafting of maleic anhydride onto polypropylene¹¹, maleic anhydride and acrylonitrile butadiene styrene (ABS)¹⁵ and acrylic acid onto PBD and ABS⁴.

Effect of reaction temperature: The effect of temperature on the graft yield was studied by keeping the weight of PBD, monomer (IBA/IBM) and initiator constant at 0.500, 0.600 and 0.030 g, respectively. All the reactions were performed in 100 mL reaction mixture at different temperatures using a reaction time for 6 h for IBA monomer and 4 h for IBM monomer. The variation of graft yield with temperature results are given in Table-4. The graft yield increased initially and then starts decreasing, with further increase in temperature. The increase was due to the increased decomposition of the initiator. By this the number of free radicals as well

as their mobility also increases resulting in a higher per cent of grafting. At higher temperature higher mobility also results in mutual termination of free radicals resulting decreased availability of free radicals for polymerization, hence decreasing the rate of grafting. Similar observations were made for grafting of maleic anhydride onto low density polyethylene (LDPE)¹⁶, polypropylene¹¹ and ABS¹⁵. This was supported by the results of the rate of grafting (Table-4). In the above results the graft yields of IBM are slightly less than that of a IBA. This may be attributed to the $-\text{CH}_3$ group in IBM at the double bond which cause steric hindrance for the reaction.

TABLE-3
EFFECT OF TIME ON GRAFTING OF IBA AND IBM
ONTO *CIS*-POLYBUTADIENE

Time (h)	IBA ^a grafting			Time (h)	IBM ^b grafting		
	Graft yield (%)	Graft efficiency (%)	R _g (mol L ⁻¹ s ⁻¹)		Graft yield (%)	Graft efficiency (%)	R _g (mol L ⁻¹ s ⁻¹)
1	79	65.83	47.88×10^{-5}	1	81	67.50	46.00×10^{-5}
2	95	79.16	28.79×10^{-5}	2	86	71.66	24.42×10^{-5}
4	110	91.66	16.66×10^{-5}	4	138	115.00	19.59×10^{-5}
6	126	105.00	12.72×10^{-5}	6	138	115.00	13.06×10^{-5}
8	124	103.33	9.39×10^{-5}	8	136	113.33	9.65×10^{-5}
10	124	103.33	7.51×10^{-5}	10	137	114.16	7.78×10^{-5}
12	126	105.00	6.36×10^{-5}	12	134	111.66	6.34×10^{-5}
14	125	104.16	5.41×10^{-5}	14	131	109.16	5.31×10^{-5}

^a0.500 g PBD, 0.600 g IBA, 0.030 g BPO in 100 mL at 70°C.

^b0.500 g PBD, 0.600 g IBM, 0.030 g BPO in 100 mL at 70°C.

TABLE-4
EFFECT OF TEMPERATURE ON GRAFTING OF IBA AND IBM
ONTO *CIS*-POLYBUTADIENE

Temp. (°C)	IBA ^a grafting			Temp. (°C)	IBM ^b grafting		
	Graft yield (%)	Graft efficiency (%)	R _g (mol L ⁻¹ s ⁻¹)		Graft yield (%)	Graft efficiency (%)	R _g (mol L ⁻¹ s ⁻¹)
50	18	15.00	1.81×10^{-5}	50	20	16.66	2.83×10^{-5}
60	102	85.00	10.30×10^{-5}	60	114	95.00	16.18×10^{-5}
70	126	105.00	12.72×10^{-5}	70	138	115.00	19.59×10^{-5}
80	147	122.50	14.85×10^{-5}	80	165	137.50	23.42×10^{-5}
90	151	125.83	15.25×10^{-5}	90	149	124.16	21.15×10^{-5}
100	133	110.83	13.43×10^{-5}	100	121	100.83	17.18×10^{-5}
110	110	91.66	11.11×10^{-5}	110	70	58.33	9.93×10^{-5}
120	40	33.33	4.04×10^{-5}	120	50	41.66	7.09×10^{-5}

^a0.500 g PBD, 0.600 g IBA, 0.030 g BPO in 100 mL for 6 h.

^b0.500 g PBD, 0.600 g IBM, 0.030 g BPO in 100 mL for 4 h.

Thermogravimetric analysis: Thermal stability of the homo and graft copolymers are determined using VSIA Dupont 2000 thermal analyzer at a heating rate of 10°C/min. The relative thermal stabilities are evaluated by the comparison of the initial decomposition temperature (IDT) and the decomposition temperature of 50 % weight loss (T 50 %). In these copolymers, the factors that can influence thermal stability are: (a) back bone structure (b) nature of acrylate and methacrylate and (c) PBD content. The TG analysis has been conducted on the homopolymers, *viz.*, poly isobornyl acrylate (PIBA), poly isobornyl methacrylate (PIBM) and *cis*-polybutadiene (PBD) and also on the graft polymers. The TGA curves are shown in Fig. 1 and the results are tabulated in Table-5 for the homo and graft copolymers. The results show that the degradation of graft copolymers is intermediate between that of the two homopolymers which suggests that the two polymers degrade with no interaction between the degradation pathways¹⁷.

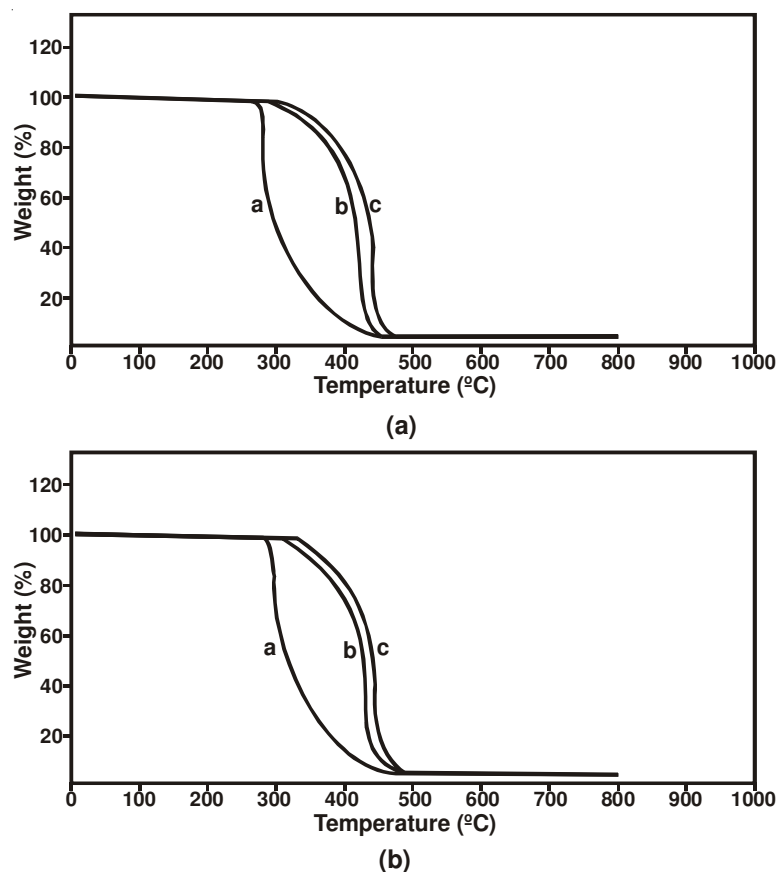


Fig. 1. (a) TGA curves (a) PIBA (b) PBD-g-IBA (60 %) (c) PBD
(b) TGA curves (a) PIBM (b) PBD-g-IBM (56 %) (c) PBD

TABLE-5
THERMAL BEHAVIOUR OF HOMO AND GRAFT COPOLYMERS

System	IDT (°K)	T _{50%} (°C)
Homo PIBA	281	302
Homo PIBM	285	314
Homo PBD	340	446
PBD-gr-IBA	311	425
PBD-gr-IBM	317	428

Site of the reaction onto PBD: Nai-Jan and Sunberg¹ studied the grafting reactions of different vinyl monomers onto *cis*-PBD and they observed that the active monomers will attack at a vinylic position of PBD and will give graft copolymer. Whereas the inactive monomers will attack on the double bond of the PBD and give the graft copolymers by this route. According to their hypothesis since vinylic radical formed due to the abstraction of vinylic hydrogen of the PBD by the primary radical is resonance stabilized, only the active monomers are able to attack on the vinylic position then producing graft copolymer, whereas inactive monomers initially from monomer radicals by the reaction with primary radical. These monomer radicals will attack on the double bond position of PBD and will give the graft copolymer¹⁷. In the present study IBA and IBM were grafted onto PBD. The formation of graft copolymers as well as the site of grafting were confirmed from IR spectra.

IR spectra

Infrared spectra of the ungrafted PBD, grafted samples of PBD-gr-IBA and PBD-gr-IBM were recorded on a Perkin-Elmer model BX-spectrophotometer in 4000-500 cm⁻¹ range with KBr pellets.

The IR spectra of PBD-gr-IBA¹⁸ shows the C–H out-of-plane bending vibrations at 999, 916, 750 cm⁻¹ and the olefinic C–H stretching vibration at 3005 cm⁻¹. These band intensities have been decreased with increase in graft yield. A new band is observed at 1750 cm⁻¹ due to the entry of ester carbonyl group showing that isobornylacrylate has been introduced as a graft onto PBD. From the earlier observations^{4,18} and the observations of IR spectrum of the ungrafted PBD and PBD-gr-IBA copolymers in the present study, it can be concluded that grafting occurred on the double bond position of the PBD.

In the case of PBD-gr-IBM, the IR spectra shows in addition to the above peaks at 3005, 999, 916 and 750 cm⁻¹, a new peak at 1730 cm⁻¹, which is due to the entry of ester carbonyl group, showing the IBM has been produced as a graft onto PBD. From the earlier observations and the observation¹⁸ of IR spectrum of ungrafted PBD and grafted PBD-gr-IBM

copolymers it can be concluded that the grafting occurred on the vinyllic position of the PBD.

Viscosity measurements

The intrinsic viscosity of graft copolymerization have been determined for both monomers IBA/IBM¹⁹. With an increase in the concentration of the monomer and temperature the rate of grafting increase up to some extent and then remains almost constant. This trend is inversely related to intrinsic viscosity measurements. The results are shown in Table-6 for monomers and in Table-7 for temperature.

TABLE-6
EFFECT OF CONCENTRATION OF MONOMERS IBA/IBM ON
INTRINSIC VISCOSITY (η)

Concentration of monomer IBA/IBM	IBA		IBM	
	Rg (mol L ⁻¹ s ⁻¹)	η (dL/g)	Rg (mol L ⁻¹ s ⁻¹)	η (dL/g)
0.075	1.47×10^{-5}	1.45	1.30×10^{-5}	1.38
1.500	3.69×10^{-5}	1.39	3.17×10^{-5}	1.32
0.300	14.50×10^{-5}	1.31	11.94×10^{-5}	1.29
0.600	33.82×10^{-5}	1.28	29.64×10^{-5}	1.12
0.900	40.29×10^{-5}	1.27	35.74×10^{-5}	1.07
1.200	45.18×10^{-5}	1.25	39.68×10^{-5}	1.05

TABLE-7
EFFECT OF REACTION TEMPERATURE ON INTRINSIC
VISCOSITY (η) WITH IBA/IBM

Temperature	IBA		IBM	
	Rg (mol L ⁻¹ s ⁻¹)	η (dL/g)	Rg (mol L ⁻¹ s ⁻¹)	η (dL/g)
60	10.30×10^{-5}	1.27	16.18×10^{-5}	1.25
70	12.72×10^{-5}	1.20	19.59×10^{-5}	1.17
80	14.85×10^{-5}	1.06	23.42×10^{-5}	1.02
90	15.25×10^{-5}	1.98	21.15×10^{-5}	1.09
100	13.43×10^{-5}	1.03	17.18×10^{-5}	1.20
110	11.11×10^{-5}	1.18	–	–

The explicit behaviour of the inversely proportional variation of the intrinsic viscosity with increase in rate of grafting might be due to the reason that as percentage of monomer composition is more than that of the back bone polymer, molecular weight of grafted polymer is decreasing. The temperature effect can be explained by the fact that as the reaction temperature increases the number of available free radicals as well as their

mobility increases, thereby more amount of the back bone polymer participates in the reaction to give highly viscous product. As the temperature increases, higher mobility of the free radicals results in decreased availability of free radicals to give less viscous product, hence of less molecular weight.

A different behaviour has been observed in the case of increase in the concentration of initiator and reaction time. As the concentration of the initiator and reaction time increases the rate of grafting increases up to some extent and then remains constant. The trend is directly reflected in the intrinsic viscosity values of grafted copolymers as shown in Table-8 for initiator and Table-9 for reaction time.

TABLE-8
EFFECT OF CONCENTRATION OF THE INITIATOR ON INTRINSIC VISCOSITY (η) WITH IBA/IBM

Concentration initiator	IBA		IBM	
	Rg (mol L ⁻¹ s ⁻¹)	η (dL/g)	Rg (mol L ⁻¹ s ⁻¹)	η (dL/g)
0.010	16.06×10^{-5}	0.95	13.91×10^{-5}	1.17
0.020	22.42×10^{-5}	1.04	22.15×10^{-5}	1.25
0.030	28.79×10^{-5}	1.18	22.42×10^{-5}	1.29
0.040	29.09×10^{-5}	1.19	23.85×10^{-5}	1.27
0.050	28.18×10^{-5}	1.18	24.70×10^{-5}	1.29
0.060	27.58×10^{-5}	1.16	23.28×10^{-5}	1.29

TABLE-9
EFFECT OF REACTION TIME ON INTRINSIC VISCOSITY (η) WITH MONOMERS IBA/IBM

Reaction time (h)	IBA		IBM	
	Rg (mol L ⁻¹ s ⁻¹)	η (dL/g)	Rg (mol L ⁻¹ s ⁻¹)	η (dL/g)
2	28.79×10^{-5}	1.18	24.42×10^{-5}	1.25
4	16.66×10^{-5}	1.15	19.59×10^{-5}	1.17
6	12.72×10^{-5}	1.07	13.06×10^{-5}	1.12
8	–	–	9.65×10^{-5}	1.07
10	7.51×10^{-5}	1.01	–	–
12	6.36×10^{-5}	0.98	6.34×10^{-5}	1.01

The reason for this type of behaviour for initiator might be attributed to the constant proportional participation of back bone polymer and the monomer in the reaction. This type of behaviour for reaction might be due to the reason that after an optimum reaction time the proportion of back

bone polymers and the monomer participating in the reaction remaining constant which has been reflected in the intrinsic viscosity values.

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