A gel permeation chromatography method to determine grafting efficiency during graft copolymerization

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A new method of measuring the efficiencies of free radical grafting reactions is presented. This technique utilizes the compositional analysis capability of dual-detector (ultraviolet and refractive index) gel permeation chromatography (g.p.c.) in which the mixture of polymers resulting from the graft copolymerization reaction is also subjected to separation by molecular size. Samples of the reaction mass drawn from a reactor are diluted with g.p.c. eluent and injected directly into the chromatograph without any other preparative step. Grafting efficiency, graft ratio, molecular weight distributions and the frequency of graft chains along the backbone polymer are simultaneously determined. Low molecular weight diluents (residual monomer, solvent, initiator, etc.) are readily separated from the polymer within the chromatograph, allowing for the determination of the fractional conversion of graft monomer (to grafted and ungrafted polymer) from the same analysis. This simple technique overcomes the need to separate or purify the polymer mixture prior to analysis, as required for most other methods. Experimental results are presented for the grafting of styrene onto *cis*-polybutadiene. Gelled samples cannot be analysed by this new technique.

(Keywords: gel permeation chromatography; grafting efficiency; graft copolymerization)

INTRODUCTION

Graft copolymers are important technological materials in that they can greatly influence the interfacial region in polymer blends and composites. Among the graft polymers derived from the free radical mechanism, commercially important examples are acrylonitrile butadiene styrene (ABS), high impact polystyrene (HIPS) and rubber-toughened polyester. In such polymerizations it is extremely important to be able to determine the characteristics of the graft copolymer resulting from the process, yet it has always been difficult to achieve. One of the more common tests applied to the polymer resulting from the grafting process has been the so-called 'graft efficiency' analysis. This term is consistently defined as the percentage of the grafting monomer which is ultimately bonded to the backbone polymer, the remainder being unattached, or 'free', polymer. Other features of the grafted copolymer molecule that are of interest are the graft ratio (mass of grafted polymer to mass of backbone polymer) and the molecular weight of the grafted chains. The graft frequency (number of repeat units between graft points) is readily computed once the above parameters are known.

The most common technique used to determine the graft efficiency has involved selective solvent extraction of the 'free polymer' from a mixture of grafted backbone polymer, ungrafted backbone polymer and free polymer[1,2]. Although this technique has been found to yield reproducible results, one can never be sure that complete extraction is achieved. Other techniques such as selective polymer precipitation from dilute solution[3] and thin layer chromatography[4] have also been reported, with each method having its own limitations and reliability, especially for high molecular weight samples. Crosslinked polymer presents a difficult problem for all of the analysis techniques.

The purpose of this paper is to describe a newly developed test method for graft copolymer analysis which makes use of the compositional analysis capability of dual-detector gel permeation chromatography (g.p.c.). Utilizing refractive index (r.i.) and ultraviolet light absorption (u.v.) detectors, g.p.c. has been shown to be a sensitive technique for the analysis of composition in polymer blends and copolymers[5,6], particularly for the dependence of composition on molecular weight. We describe here the application of this technique for graft copolymers synthesized via free radical solution polymerization. In particular, the goal was to develop a technique that allowed for the direct injection into the chromatograph of a sample withdrawn from the reactor at any time without having to separate the polymer from the residual monomer and solvent prior to analysis. Previous experience has led us to the conclusion that such a preparative step, although simple in concept, can lead to alterations (e.g. oxidation, crosslinking) in molecular structure, and we sought to avoid these. Furthermore, it will be shown that the g.p.c. analysis of such reactor samples can also yield measurements for the extent of monomer conversion during reaction.

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CAPABILITIES OF G.P.C. FOR COMPOSITIONAL ANALYSIS

As noted above, the synthesis of graft copolymers yields a mixture of three different polymers: graft copolymer, free polymer and ungrafted backbone polymer. This has all of the characteristics of polymer blends which can be analysed via g.p.c. compositional procedures[5,6]. Here the method makes use of the different u.v. absorptions and r.i. values of different polymers, and in combination with the molecular size separation achieved in the g.p.c. columns allows for compositional/molecular weight analysis. As applied to graft copolymer analysis via g.p.c., the key is first to get the two components of the second-stage polymer (grafted and free) separated from one another by molecular size differences. Then the compositional analysis can be performed for the two fractions: one containing graft copolymer and ungrafted backbone polymer (if any), and the other containing free, postformed polymer. The simplest situation arises when the backbone polymer has a substantially higher chain length than the grafted polymer or free polymer. The discussion in this paper will be limited to those systems in which the backbone polymer has a relatively high molecular weight and the grafted (and free) polymer has a significantly lower molecular weight. This is quite readily achieved by using the solution polymerization technique to carry out the grafting reaction. Here the reactor contents can be readily sampled (unless gelation through crosslinking takes place) and injected directly into the chromatograph where the high and low molecular weight polymers can be separated from one another and also from the residual monomer and solvent.

EXPERIMENTAL

Polymerization system

As already mentioned, free radical solution polymerization was conducted with moderate to high molecular weight backbone polymer separately prepared or purchased. That polymer along with the grafting monomer and oil soluble initiator was dissolved in a suitable solvent and placed in glass capillary tubes. These tubes (5 mm outside diameter with a 1 mm wall thickness) were sealed under vacuum at −30°C, stored (for no longer than 0.5 h) at ~5°C and then placed within an oil bath operating at 60°C. This commonly used reactor technique offers excellent reactant fluid temperature control even for reactions reaching completion within 30 min – those described in this paper required a day or longer to complete. Multiple tubes were prepared for each experiment and each in turn was sacrificed to provide a sample for analysis at a chosen time. The reaction was quenched by plunging the sealed tube into cold water, and a measured weight of the sample was removed and diluted into a known amount of g.p.c. solvent containing a very small quantity of inhibitor.

Materials

The overall grafting study, which we will report in subsequent papers, involved a variety of backbone polymers, grafting monomers and oil soluble initiators. The results chosen for discussion in this paper are limited to a *cis*-polybutadiene (*cis*-PBD) backbone (Scientific Polymer Products, catalogue number 206, $\bar{M}_n = 96\,900$, $\bar{M}_w = 279\,500$, $\bar{M}_w/\bar{M}_n = 2.68$ as determined by the supplier) grafted with styrene monomer (Aldrich Chemical Company). The styrene monomer was scrubbed with 5 wt% aqueous NaOH to remove the inhibitor prior to use. Benzoyl peroxide (BPO) and 2,2′-azobisisobutyronitrile (AIBN) (Polysciences) were used as received. Benzene (J. T. Baker Chemical Company) was used as the solvent to avoid as much as possible the chain transfer to solvent reaction. Tetrahydrofuran (THF) (Fisher, high performance liquid chromatography grade) was used as the eluent for g.p.c. analysis. Hydroquinone (J. T. Baker Chemical Company) was dissolved in methanol (J. T. Baker Chemical Company) at 1 wt% and two drops were added to each reactor sample prior to g.p.c. analysis.

G.p.c. instrument and procedures

The g.p.c. chromatograph was obtained from Millipore Corporation. The differential refractometer was a Waters series R-400 and the u.v. detector was a Waters series 486. Three Ultrastyragel g.p.c. columns were placed in series in the sequence 10^5 Å, 10^4 Å, 10^3 Å. A temperature controller maintained column temperatures at 25°C and the computer software package MAXIMUM-820 by Waters was used for molecular weight analyses. Portions (250 μl) of dilute polymer solutions (approximately 0.1 wt% polymer) were injected into the chromatograph for each analysis. The solvent flow rate was always 1 ml min^{-1}, and the u.v. detector was set at a wavelength of 254 nm for all analyses. Both detector responses were calibrated for *cis*-PBD and polystyrene (PS) by injecting 250 μl portions of variable homopolymer concentration solutions into the chromatograph. The calibration amounts to developing the relationship between the microvolt signal of the detector (for r.i. and u.v.) and known masses of either *cis*-PBD or PS. Such calibrations are excellent, linear relationships when done carefully and are not dependent upon polymer molecular weight[7,8] as long as it is above 2000. By knowing that the measured detector response at any retention time (or retention volume) is the result of a combination of at most two polymeric species, the detector calibration curves can be used to compute the polymer composition at any point in the chromatogram. Example calculations will be presented later. Those which involve molecular weight determination were dependent upon calibration of the instrument with narrow molecular weight polystyrene standards (purchased from Scientific Polymer Products).

Data analysis

Figure 1 shows g.p.c. chromatograms for a reactor sample taken at the start of the reaction in which BPO was used as the initiator. These represent signal responses from the r.i. and u.v. detectors, and demonstrate the inability of the u.v. detector to respond to the *cis*-PBD backbone. Monomer, solvent and inhibitor are easily separated from the *cis*-PBD, eluting at about 1800 s after injection.

Figures 2 and *3* show the respective r.i. and u.v. detector responses for a sample withdrawn from the temperature bath during the reaction. The u.v. response clearly shows that grafting has taken place, as the 'free' polystyrene (PS) has a low molecular weight (MW) and a peak elution time of about 1350 s, while the low MW grafted PS chains elute with the *cis*-PBD to which they must be attached.

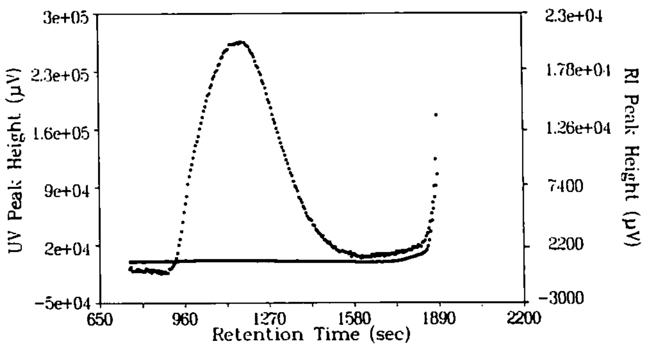

Figure 1 R.i. (broken line) and u.v. (continuous line) chromatograms at 0% conversion of styrene

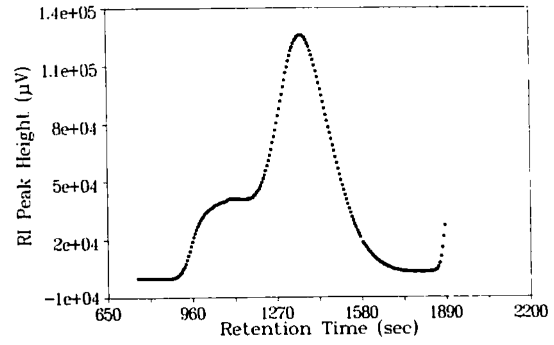

Figure 2 R.i. chromatogram at 36% conversion of styrene

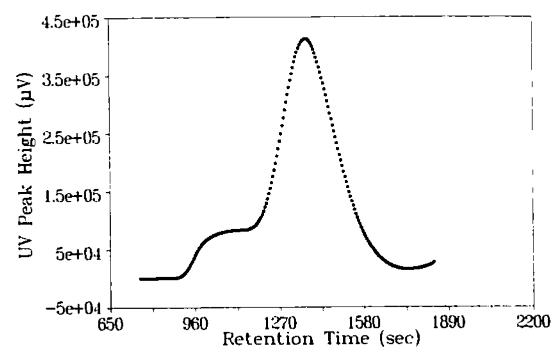

Figure 3 U.v. chromatogram at 36% conversion of styrene

In order to prove that the benzoyl peroxide initiator fragments (which are possibly incorporated into the polymer backbone or grafted polymer) do not influence our results, we have run several experiments. The first was to 'react' the *cis*-PBD in benzene solution with BPO for the same period of time as that used for the styrene-grafting reaction. The results are displayed in *Figures 4* and *5* where the u.v. responses are shown at two different scales. *Figure 4* indicates that some BPO fragments are incorporated within the *cis*-PBD backbone since the u.v. absorption increases significantly during the reaction. Furthermore, the *cis*-PBD molecular weight distribution appears to broaden with time and the reacting mass eventually gelled. The ability to detect initiator end-groups in this manner is consistent with the results shown by Garcia-Rubio *et al.*[9] in their work with polystyrene synthesized with BPO. Clearly, the BPO fragment content in the *cis*-PBD of *Figure 4* cannot be very large, and when the ordinate scale is changed to reflect that used in our graft copolymer detection method (as in *Figure 3*) it is essentially impossible to measure the BPO content of the *cis*-PBD, as in *Figure 5*. Further evidence of this initiator fragment effect is shown in *Figure 6* where poly(methyl methacrylate) (PMMA) produced in benzene solution is depicted by both r.i. and u.v. detector responses with the ordinate scale at the same level as used in our graft measurements. Although the BPO fragments can be seen in the u.v. response at higher detector sensitivities, they are insignificant at the sensitivity level utilized in our grafting studies. With the above evidence, the BPO fragments which may be present in the samples of interest can safely be neglected. When AIBN is used as the initiator, this type of concern is not there in the first place.

In the best of circumstances one can probably achieve complete separation of the free, or ungrafted, polymer

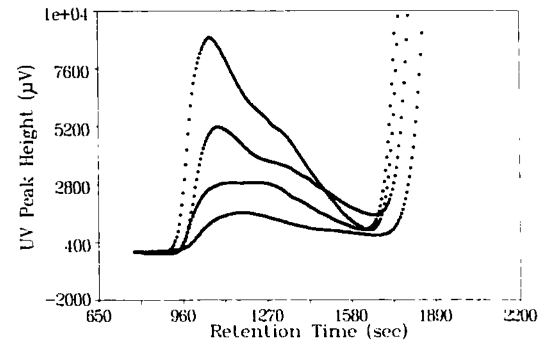

Figure 4 U.v. chromatograms of BPO reacted with *cis*-PBD at 0, 18, 45 and 95 h

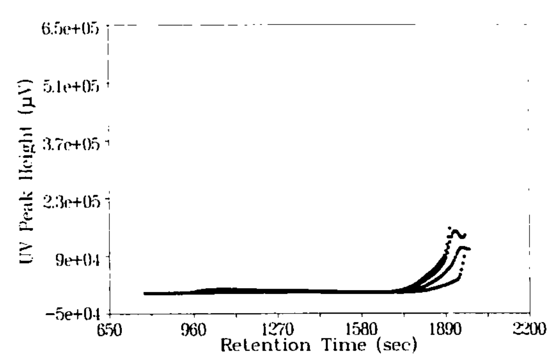

Figure 5 U.v. chromatograms of BPO reacted with *cis*-PBD at 0, 18, 45 and 95 h

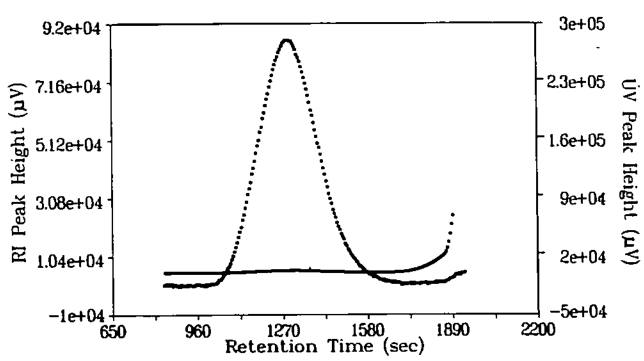

Figure 6 R.i. (broken line) and u.v. (continuous line) chromatograms of PMMA initiated by BPO

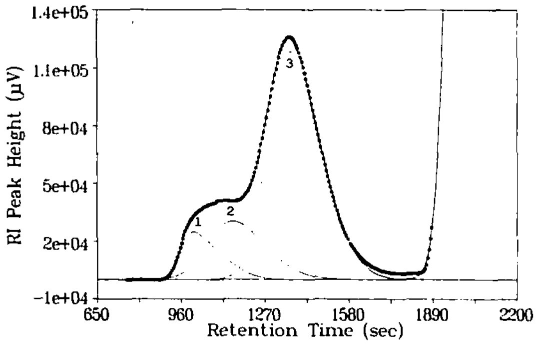

Figure 7 R.i. chromatogram at 36% conversion of styrene with peak fitting

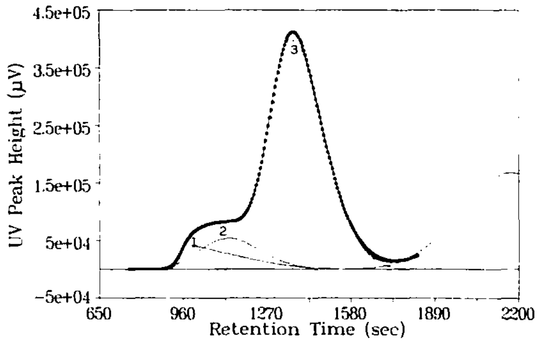

Figure 8 U.v. chromatogram at 36% conversion of styrene with peak fitting

from both the backbone and the residual monomer and solvent. In the case of *Figures 2* and *3* this has not happened and one needs to resort to a peak-fitting analysis in order to distinguish between overlapping areas of the peaks prior to compositional analysis. This was accomplished in our case by the use of Peakfit commercial software[10] to determine the individual distributions, followed by compositional analysis of these distributions[5].

Figures 7 and *8* show the peak-fitting analyses for the chromatograms of *Figures 2* and *3* at 36% conversion of styrene monomer. Note that the backbone polymer (both grafted and ungrafted, if any) is best fitted by a combination of two distributions, while the free polymer is well described by a single distribution, as expected.

The procedure for the peak-fitting analysis is briefly described as follows. The u.v. and r.i. peak data were first generated by MAXIMUM-820 software and then transferred to Peakfit software. After that, these peaks were fitted by the non-linear regression function in the Peakfit software. The results of these peak fittings were then printed out as in *Figures 7* and *8*. Note that peaks 1 and 2 in *Figures 7* and *8* are the peak fittings for both the graft copolymer (PS grafted onto *cis*-PBD) and non-grafted *cis*-PBD, if any. Peak 3 is the free homopolystyrene that was formed during the solution polymerization and not grafted onto *cis*-PBD.

APPLICATION TO GRAFT COPOLYMERIZATION

As mentioned above, the system chosen for study here was that of a *cis*-PBD backbone polymer grafted with styrene in benzene solution. Both BPO and AIBN were used as initiators and the reactions were conducted in the batch mode at 60°C. The g.p.c. method can be used to determine the conversion of reacting monomer, the grafting efficiency, the graft ratio and the molecular weight distributions (and averages) of both the grafted and free polymer, although the grafted polymer may be mixed with ungrafted backbone polymer within the same distribution. If one can legitimately make the assumption that the graft chain lengths are on average equal to the free polymer chain lengths, then one can determine the graft frequency as well. All of this may be obtained from a single injection of the THF-diluted reactor sample.

Table 1 shows the experimental formulation used. This constitutes a rather dilute solution of backbone polymers and grafting monomer and assumes that relatively low viscosities are maintained throughout the reaction and that phase separation is prevented as the second-stage polymer is formed. In the bulk polymerization mode this formulation would result in high viscosity and phase separation very early in the reaction.

Calculation of monomer conversion

The monomer conversion is defined as the mass of PS formed (grafted and free) divided by the initial mass of monomer. For the reaction conditions of the above formulation the reaction is rather slow and a sample withdrawn at 60 h of reaction time (the half-life of BPO at 60°C is about 65 h) resulted in the chromatograms displayed in *Figures 7* and *8*. The polymer peaks in the u.v. chromatogram correspond solely to PS as the u.v. absorbance of the *cis*-PBD backbone is negligible (see *Figure 1*). After applying the peak-fitting routine and integrating the area under each distribution, the amount of PS in the sample can be determined from the calibration data for PS. In this case the conversion of styrene monomer to PS (both grafted and free) is computed to be 35.9%. Gravimetric analysis of the same sample yielded a conversion of 33.5%, although we had some concern for the oxidation of the *cis*-PBD during the air drying at 65°C. Gas chromatography could also be used to measure monomer conversion, but the g.p.c. method described here avoids the need for such a separate analysis.

Calculation of grafting efficiency

The grafting efficiency is readily defined as the mass of the grafted PS divided by the total PS produced. This may be viewed as an instantaneous value (i.e. resulting from reactions occurring at a particular time during the reaction) or as a cumulative value. The latter version is the one that can be measured, as the polymers in the sample are the result of reactions taking place from the very beginning of the process. Using the data determined

Table 1 Formulation for grafting experiment GBDS-15

Component		Weight (g)	Content (wt%)	Concentration (mol l^{-1})
Backbone	(*cis*-PBD)	0.3069	1.4119	0.2273
Initiator	(BPO)	0.0166	0.0764	2.74×10^{-3}
Monomer	(styrene)	3.4217	15.7420	1.3160
Solvent	(benzene)	17.9909	82.7697	9.2261

from the analysis of *Figure 8* as just discussed, the cumulative grafting efficiency of the sample is 20.4%.

Calculation of graft ratio

The graft ratio is the mass of grafted PS per unit mass of backbone polymer. This must be considered to be an average value for all backbone chains as there may possibly be some *cis*-PBD chains that do not have any PS grafted to them. The present technique does not separate these two types of backbone polymer, if they exist. In the present example, the PS of interest is that shown only in the high molecular weight peak of *Figure 8*. The mass of *cis*-PBD backbone injected into the chromatograph is known from the sample weight, and the resultant computation yields a graft ratio of 0.82 g PS per gram *cis*-PBD.

Calculation of free PS chain length

The ungrafted PS is clearly evident in the low molecular weight peak, eluting at about 1350 s. After appropriate peak fitting, this distribution was analysed for molecular weight parameters using the MAXIMUM-820 software supplied with the chromatograph and utilizing the results from column calibrations with a narrow distribution PS standard (Scientific Polymer Products). For this example the analysis of the free PS yields $\bar{M}_n = 28\,300$, $\bar{M}_w = 47\,620$, $\bar{M}_z = 68\,530$ and $\bar{M}_w/\bar{M}_n = 1.68$.

Calculation of graft frequency

The conditions of low viscosity throughout the reaction without phase separation make it likely that the MWs of the grafted and free chains will be the same. It is judged that the propagation and termination rates of grafted and free polymer radical chains would be the same in the dilute solution environment. Given this assumption it is possible to compute a graft frequency by knowing the total numbers of graft chains and backbone chains, both derived from the molecular weight analysis of each, the latter being done prior to any reaction. For this example we found 3.9 mg of grafted PS at an $\bar{M}_n$ of 28 300 and 4.8 mg of *cis*-PBD at an $\bar{M}_n$ of 96 880. By assuming that all the backbone *cis*-PBD chains have the same 1794 repeat units and all grafted PS has the same 272 repeat units, one can compute that the average backbone chain has 2.8 chains of PS grafted to it. This translates to a graft frequency of 641 repeat units between graft sites. The details of all of the above calculations are shown in the Appendix.

Variation of grafted properties with reaction time

Figure 9 shows the superimposed u.v. chromatograms for several sequential samples withdrawn from the reactor, including the zero time sample. Here it is readily apparent that the absolute quantity of grafted PS (i.e. the graft ratio) increases significantly as the reaction progresses, but one cannot very well perceive the variation in grafting efficiency without quantitative analysis. The calculated results for samples at 15, 22, 36 and 51% monomer conversion are displayed in *Table 2*.

It is obvious from the results shown in this table that while the graft ratio and graft frequency are strong functions of conversion (as expected in any case in which a reasonable amount of grafting takes place), the grafting efficiency is relatively constant. This suggests that for this system the relative propensities for monomer consumption by grafted and free PS radicals are not significantly dependent upon monomer concentration. This clearly indicates something about the dominating reactions within the series of reactions that take place in free radical grafting. However, not all combinations of backbone polymers, monomers and initiators yield such results and one must avoid making hasty conclusions about the graftability of any particular combination of backbone polymer and grafting monomer. A good example of this is shown in *Figure 10* which displays the grafting behaviour for the formulation shown in *Table 3*. Note that AIBN was used in place of BPO as

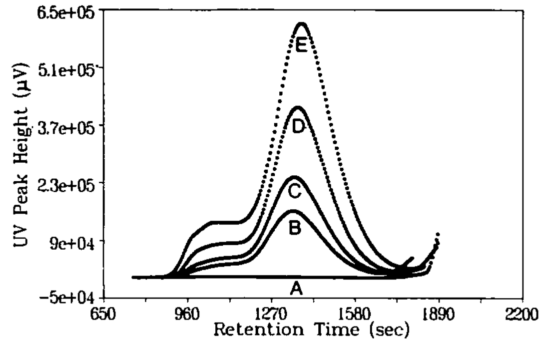

Figure 9 U.v. chromatograms at (A) 0, (B) 15, (C) 22, (D) 36 and (E) 51% conversion of styrene with benzoyl peroxide

Table 2 Grafting results of experiment GBDS-15

	Monomer conversion (%)				
Graft parameter	0	15	22	36	51
Grafting efficiency (%)	–	20.01	20.23	20.40	21.99
Graft ratio (g g^{-1})	0	0.28	0.46	0.82	1.20
$\bar{M}_n$ of free PS	0	29 000	28 500	28 300	28 000
Graft frequency (repeat units between graft sites)	–	1725	1146	641	368

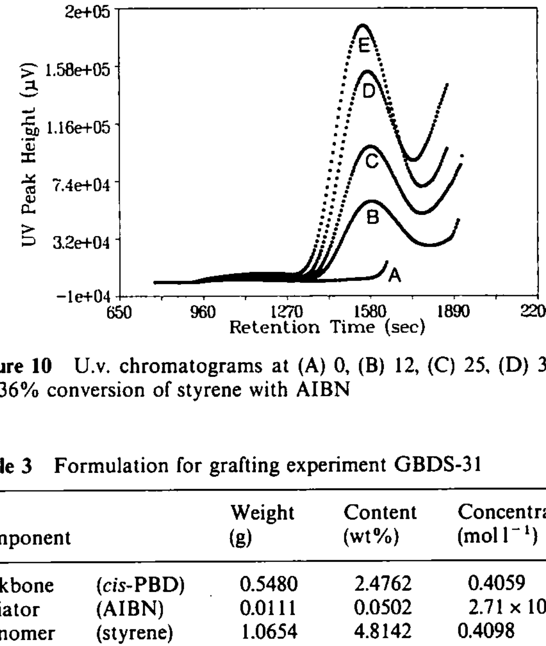

Figure 10 U.v. chromatograms at (A) 0, (B) 12, (C) 25, (D) 31 and (E) 36% conversion of styrene with AIBN

Table 3 Formulation for grafting experiment GBDS-31

Component		Weight (g)	Content (wt%)	Concentration (mol l^{-1})
Backbone	(*cis*-PBD)	0.5480	2.4762	0.4059
Initiator	(AIBN)	0.0111	0.0502	2.71×10^{-3}
Monomer	(styrene)	1.0654	4.8142	0.4098
Solvent	(benzene)	20.5060	92.6595	10.5159

the initiator. Furthermore, the monomer to backbone polymer ratio was reduced for better grafting (this will be demonstrated in a future paper). Here it is quite evident that very little grafting has taken place. The grafting efficiency was computed to be about 3% and quite constant as conversion increased.

CONCLUDING REMARKS

While such a distinction between the grafting results for *cis*-PBD and styrene using BPO as compared to AIBN has been known for some time[11–14], it is quite possible to graft other monomers (such as acrylics) onto *cis*-PBD using AIBN as the initiator. Such a result must indicate a shift in one or more of the reactions dominating the overall grafting process, a subject which we will discuss in a forthcoming series of papers. Our intent in the present paper was to demonstrate the great simplicity and utility of the dual-detector g.p.c. method for measuring the characteristics of free radical graft copolymerizations. The present state of development of this method is limited to situations in which the free, postformed polymer is of sufficiently lower molecular weight than the backbone polymer so that the two can reasonably be separated by size prior to compositional analysis. A further, but obvious, limitation is that one cannot analyse gelled samples by this technique.

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APPENDIX

Calculation of monomer conversion

The definition of conversion of monomer is

$$\text{conversion} = \frac{\text{PS formed}}{\text{initial mass of monomer in sample}}$$

The total weight of styrene monomer in 0.3409 g of a zero conversion sample is, via *Table 1*, 0.3409 g × 15.7420% = 53.7 mg. From the u.v. chromatogram (*Figure 8*), the total u.v. peak area of polystyrene is area(peak 1 + peak 2 + peak 3) = $0.9942 + 1.498 + 9.772) \times 10^7 = 12.2142 \times 10^7$ (μV s). By applying the method described in the literature[5], the total weight of PS formed is 19.26 mg. Therefore, the conversion of styrene monomer = (19.26/53.7) × 100% = 35.87%.

Calculation of grafting efficiency

The definition of grafting efficiency (Φ) is

$$\Phi \equiv \frac{\text{weight of grafted PS}}{\text{weight of free PS} + \text{weight of grafted PS}}$$

From the u.v. chromatogram

$$\Phi = \frac{\text{area(peak 1 + peak 2)}}{\text{area(peak 1 + peak 2 + peak 3)}}$$

$$= \frac{0.9442 + 1.4498}{0.9442 + 1.4498 + 9.772}$$

$$= 20.40\%$$

Calculation of graft ratio

The weight of backbone *cis*-PBD in 0.3409 g of the sample should be (via *Table 1*) 0.3409 g × 1.4119% = 4.8 mg. The total weight of PS in the sample can be calculated from the conversion data calculated earlier, i.e. 53.7 mg × 35.87% (conversion) = 19.26 mg. The weight of grafted PS can be calculated by using the grafting efficiency data from the previous section, i.e. 19.26 mg × 20.40% (graft efficiency) = 3.9 mg. Therefore

$$\text{graft ratio} = \frac{\text{weight of grafted PS}}{\text{weight of backbone } cis\text{-PBD}} = \frac{3.93}{4.8} = 0.82$$

Calculation of graft frequency

The graft frequency is the number of backbone polymers repeat units between graft chains. To obtain this we first calculate the number of graft chains per backbone chain. For 3.9 mg of grafted PS at an $\bar{M}_n$ of 28 300 (via *Table 2*) and 4.8 mg of grafted *cis*-PBD at an $\bar{M}_n$ of 96 880 (as noted in the Experimental section), one chain of PS has 272 (28 300/104) repeat units and one chain of *cis*-PBD has 1794 (96 880/54) repeat units. Hence, the total number of grafted PS chains is $(3.9 \times 10^{-3}/104/272)$ × (Avogadro's number) or 1.38×10^{-7} × (Avogadro's number). The total number of grafted *cis*-PBD chains is $(4.8 \times 10^{-3}/54/1794)$ × (Avogadro's number) or 0.495×10^{-7} × (Avogadro's number). The number of grafted chains per backbone chain is 1.38/0.495 = 2.8. The number of repeat units between graft sites is (1794/2.8) = 641.