Notes to the Editor

Examination of a cellulose tricarbanilate–polystyrene copolymer produced by radiation grafting

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INTRODUCTION

In previous communications[1,2] we have reported on kinetic features of the graft copolymerization of styrene to regenerated cellulose by the mutual γ-irradiation technique, and have also shown[3] how these features are affected by partial carbanilation of the cellulose prior to irradiation. The reaction products consist of polystyrene homopolymer and cellulose–styrene copolymer of which the former can be removed by extraction. Separate portions of the copolymer may be (a) hydrolysed to yield the polystyrene grafts[4] and (b) extracted with Cadoxen to remove ungrafted cellulose and leave an ostensibly pure copolymer, complete carbanilation of which produces a readily soluble cellulose–tricarbanilate copolymer (CTC–PS).

A preliminary synopsis on the characterization of CTC–PS was published some years ago[5], but the findings therein appeared abnormal in some respects. Subsequent re-examination of the results and the copolymer itself leads us to conclude that certain of the data are without true significance, since they relate to a product of ill-defined composition. Despite repeated extractions of the cellulose–styrene copolymer with Cadoxen, it is likely that there is still residual ungrafted substrate in it. Hence, essentially the data relate to a mixture of CTC–PS and cellulose tricarbanilate. Of the considerable volume of published work on radiation grafting to cellulose, only a relatively small proportion is devoted to product characterization. Hence, we consider it a useful guide to report our data here fully and to indicate where and why the inherent difficulties arise.

Radiation grafting and all physicochemical measurements were conducted at 303K. For light scattering, refractometry and differential refractometry, unpolarized light of wavelength 436 nm *in vacuo* was used. Molecular weights, denoted by M, are weight-average quantities expressed in units of kg/mol. Cellulose, polystyrene, cellulose–styrene copolymer, cellulose tricarbanilate and cellulose tricarbanilate–styrene copolymer are abbreviated respectively to CEL, PS, CEL–PS, CTC and CTC–PS.

EXPERIMENTAL

Film of regenerated CEL was immersed in styrene/water/dioxane (5/2/93 by vol) inside a glass ampoule. After outgassing by freeze–thaw cycles, the ampoule was sealed under high vacuum and subjected to γ-irradiation to a total absorbed dose of 1335 J/kg at a dose rate of 8.32×10^{-3} W/kg.

To remove PS homopolymer the film was subjected to hot extraction with benzene for 16 h in a Soxhlet apparatus and dried to constant weight *in vacuo* at 313K. Although this procedure was repeated twice, no further weight loss could be detected after that in the first extraction. The apparent degree of grafting was calculated as $(m - m_0)/m_0$, where m_0 and m are the weights of ungrafted and grafted films, respectively. Separate portions of the grafted film were treated as follows: (a) hydrolysis, as described previously[4]; (b) cold extractions under gentle agitation with Cadoxen to constant residual weight, m_g, of copolymer (three such extractions were found necessary). The true degree of grafting was calculated as $(m - m_0)/(m_g - m + m_0)$; (c) complete carbanilation of this product to yield the copolymer studied in detail. The original CEL was also carbaniiated to produce a sample of unirradiated CTC. A further sample of CTC was obtained by carbanilating[3,6] the extracted irradiated CEL, i.e. the ungrafted portion.

Specific refractive index increments, υ, were measured on a Brice–Phoenix differential refractometer calibrated with aqueous KCl. Values were obtained for solutions of PS, CTC and CTC–PS in several solvents covering a wide range of refractive index as well as in binary solvents comprising 1-bromonaphthalene and *p*-dioxane, which individually possess a high and a low refractive index respectively. Specific refractive index increments at constant chemical potential of solvents, υ_μ, were also determined for solutions in these binary solvents after attainment of dialysis equilibrium[7]. Refractive indices of single solvents, $\tilde{n}_0$, were either taken from the literature[8] or measured directly on a Pulfrich refractometer, which was used also to measure the refractive indices, $\tilde{n}_0$, of the mixed solvents. Solvents and solutions for light scattering (*LS*) were clarified by centrifugation followed by filtration through Gelman 'Solvinert' filters. Measurements were made on a Sofica photometer calibrated with purified toluene ($R_{90} = 58.1 \times 10^{-4}\mathrm{m}^{-1}$). Values of M were obtained via Zimm plots.

Thermogravimetric analysis on PS and CTC–PS was conducted on a Stanton Automatic Thermobalance at a heating rate of 0.11 K/sec and a nitrogen purge of 3.3×10^{-3} dm^3/sec within the range between ambient temperature and 973K.

RESULTS

Grafting

The apparent degree of grafting in the CEL–PS copolymer was 0.108. After extraction of ungrafted CEL the true degree of grafting was 1.79. Comparison of these figures shows that the

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Table 1 Values of $10^{-3} \times M$ (kg/mol)

LS measurement	CTC	PS	CTC–PS
Homopolymer	–	0.46	–
Graft-isolated	–	3.07	–
Copolymer in single solvents	0.43	2.45	1.06
Copolymer in selected mixed solvent	0.63	2.91	1.21
Carbanilated form of initial, unirradiated CEL	0.93	–	–
Carbanilated form of irradiated, ungrafted, extracted CEL	0.61	–	–

fraction by weight, $\widetilde{W}_g$, of the CEL which actually participates in grafting is only $[m_g - (m - m_0)]/m_0 = 0.060$. Using the true degree of grafting in conjunction with the factor 3.20 (= 519/162 = ratio of molecular weights of the segments in CTC and CEL), one obtains a value of $3.20[m_g - (m - m_0)]/\{3.20[m_g - (m - m_0)] + (m - m_0)\} = 0.64$, for the weight fraction W_A of CTC in the CTC–PS copolymer. Duplicate determinations of W_A by thermogravimetric analysis yielded values of 0.73 and 0.75 whilst duplicate elemental analysis (based on 8.09 wt% nitrogen in pure CTC) gave $W_A = 0.71$ and 0.74. Although the refractive index increments (v_A and v_B respectively) of CTC and PS in a given solvent are rather similar (see below), the measured increment v_c for the copolymer in the same solvent affords in principle a value of W_A according to equation (1).

$$v_c = W_A v_A + (1 - W_A)v_B \tag{1}$$

From measurements of v_c in methyl ethyl ketone and dioxane (which yield the largest $|v_A - v_B|$), values of 0.72 and 0.70, respectively were found for W_A. There is thus a considerable disparity of copolymer composition from the different analytical procedures. The mean value of W_A is 0.71.

Molecular weights

The molecular weights obtained by *LS* are listed in *Table 1* and the procedures adopted for their determination are summarized as follows. For PS homopolymer the same value of M was yielded with both toluene and dioxane as solvent. Dioxane was used as solvent for measurements of M for isolated PS grafts, irradiated CTC and unirradiated CTC.

In general, compositional heterogeneity in a copolymer yields an apparent value M_C^* for its molecular weight, which is related to the true molecular weights of the copolymer (M_C), of its constituent CTC portion (M_A) and of its constituent PS portion (M_B) by the equivalent expression[9] (2) and (3).

$$M_C^* = (v_A v_B/v_C^2)M_C + [v_A(v_A - v_B)/v_C]W_A M_A - [v_B(v_A - v_B)/v_C^2](1 - W_A)M_B \tag{2}$$

$$M_C^* = M_C + [(v_A - v_B)/v_C]2P + [(v_A - v_B)/v_C]^2 Q \tag{3}$$

In equation (3), P and Q are compositional heterogeneity parameters, which are defined elsewhere[9]. If $v_A = v_B$, it is seen from equations (2) and (3) that $M_C^* = M_C$, and measurements always yield the true molecular weight of the copolymer directly. Values of v_A and v_B as a function of $\tilde{n}_0$ for solutions of CTC and PS in several pure and mixed solvents are shown in *Figure 1*, which illustrates that the values of v_A and v_B are quite similar in most solvents. At the intersection of the two lines, $v_A = v_B$. However, the value of the refractive index increment at this point is rather low (~0.08 dm³/kg and it would be yielded in a solvent of $\tilde{n}_0 = 1.543$. There is no liquid of exactly this refractive index, which is a solvent for both CTC and PS. Moreover, even if there were, light scattering would yield M_C (equations 2 and 3 reduce to $M_C^* = M_C$), only, and not the additional values of M_A and M_B. The expedient of employing mixed solvents is more versatile in this respect. With mixed solvents it has been shown[10] that the relevant expressions are identical in form with equations (2) and (3) except that the refractive index increments are replaced by the corresponding quantities at constant chemical potential of solvents, $v_{\mu A}$, $v_{\mu B}$ and $v_{\mu C}$. In *Figure 2* the dependences of $v_{\mu A}$ and of $v_{\mu B}$ on $\tilde{n}_0$ are shown for binary solvents comprising various volume fractions ϕ_1 of 1-bromonaphthalene in admixture with dioxane.

The nature of the selected mixed solvents referred to in *Table 1* was dictated by salient features of *Figure 2*, viz. when $v_{\mu B} = 0$, the scattered light results solely from the CTC of a copolymer and measurements yield M_A directly. These conditions are realized by $v_{\mu A} = -0.160$ dm³/kg, $\tilde{n}_0 = 1.478$ and $\phi_1 = 0.17$. Similarly, when $v_{\mu A} = 0$, the value of M_B is yielded directly by the conditions $v_{\mu B} = 0.075$ dm³/kg, $\tilde{n}_0 = 1.458$ and $\phi_1 = 0.10$. Also, for $v_{\mu A} = v_{\mu B} = 0.140$ dm³/kg (i.e., when $\tilde{n}_0 = 1.440$ and $\phi_1 = 0.037$), the value of M_C is obtained directly from one measurement in the mixed solvent defined by these conditions. *LS* on solutions of the copolymer in several, different, single solvents yielded values of M_C^*, which differed slightly according to the refractive index of the solvent. Thus, in methyl ethyl ketone, dioxane, cyclohexanone, pyridine and nitrobenzene, M_C^* ranged from 1.28×10^3 to 0.95×10^3 kg/mol. An insufficiently wide range of values for $(v_A - v_B)/v_C$ could be afforded by this means so that it was not possible to estimate M_C [at $(v_A - v_B)/C = 0$] via the parabolic plot[9] according to equation (3). Consequently, the data were used to solve equation (2) via several combinations of simultaneous equations taking $W_A = 0.71$ for this purpose. The mean values in *Table 1* for M_C, M_A and M_B relate to this procedure.

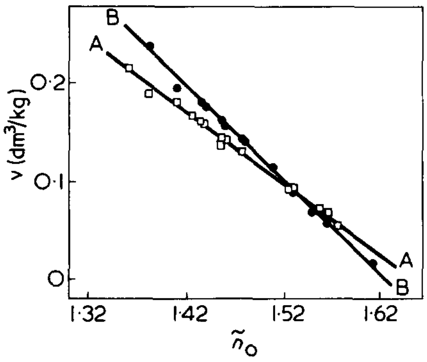

Figure 1 Specific refractive index increment at constant composition as a function of refractive index of solvent for solutions of CTC (A) and PS (B) in several pure and mixed solvents

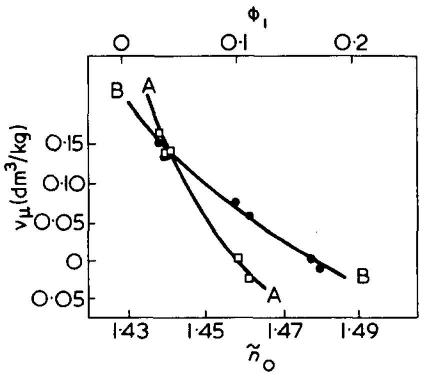

Figure 2 Specific refractive index increments at constant chemical potential as a function of refractive index of solvent for solutions of CTC (A) and PS (B) in binary mixtures of 1-bromonaphthalene (volume fraction ϕ_1) and dioxane

Selective adsorption in mixed solvents

For a polymer or copolymer in a binary solvent, the greater affinity of one of the solvents for the macromolecule produces a solvent sheaf in the immediate vicinity of the polymer, which is of a different composition from that of the bulk binary solvent. Differential refractometry is one of the methods for estimating this effect quantitatively[11], as in equation (4):

$$\gamma_1 = (\upsilon_\mu - \upsilon)/(\mathrm{d}\tilde{n}_0/\mathrm{d}\phi_1) \qquad (4)$$

Here $\mathrm{d}\tilde{n}_0/\mathrm{d}\phi_1$ is the dependence of the refractive index of the binary solvent on the volume fraction of solvent – 1; υ_μ and υ are the specific refractive index increments of the polymer at constant chemical potential and constant concentration respectively and γ_1 denotes the coefficient of selective adsorption of solvent – 1. Measurements of $\tilde{n}_0$ for sixteen different values of ϕ_1 showed that $\mathrm{d}\tilde{n}_0/\mathrm{d}\phi_1$ is constant and of value +0.270. Values of γ_1 (where solvent – 1 is 1-bromonaphthalene) were calculated via equation (4) for systems encompassing only the restricted range of ϕ_1 (0.03–0.185), which was required to obtain values of υ_μ for *LS*. Within this range, γ_1 (dm^3/kg) varies from 0 to –1.1 for solutions of CTC and from –0.1 to –0.6 for solutions of PS. Hence for both polymers there is preferential desorption of 1-bromonaphthalene, when the content of this solvent is low.

DISCUSSION

Since $|\upsilon_A - \upsilon_B|$ is small, the measured molecular weight of the CTC–PS copolymer in any solvent should not differ too appreciably from its true value. The mean value of 1.06×10^3, which is quoted in *Table 1*, is in reasonable accord with the value of $M_C = 1.21 \times 10^3$ obtained in the mixed solvent for which $\upsilon_{\mu A} = \upsilon_{\mu B}$. Allowing for the fact that the molecular weight of the PS grafts is exceptionally large, the agreement among the values obtained for M_B is also acceptable (single solvents, one mixed solvent for which $\upsilon_{\mu A} = 0$ and direct measurement on isolated graft).

The situation regarding the CTC portion is more problematic and, although an entirely satisfactory solution cannot be proposed, the following aspects have been considered: M_A (single solvents) differs from M_A (mixed solvent). The uncertainty in W_A is common to both procedures, but the use of several single solvents and simultaneous equations as well as the errors in υ_A, υ_B and υ_C comprise a greater cumulative source of error than does the method relying on one *LS* measurement in one selected mixed solvent. This, coupled with the fact that M_A (single solvent) is smaller than the molecular weight of ungrafted CTC (see *Table 1*), tends to make one place greater reliance on the value of 0.63×10^3 than on that of 0.43×10^3.

The molecular weight of the backbone of a graft copolymer is sometimes[12] identified with that of the starting material. However, statistical considerations dictate that the longer chains should participate preferentially in grafting, as we have verified[13] for a different grafting system. Calculation of the molecular weight of the grafted CTC backbone from the molecular weights of the initial and ungrafted species demands a very precise knowledge of the magnitude of $\widetilde{W}_g$. When $\widetilde{W}_g$ is very small, as is the situation here, the calculation is subject to large error. We have observed that extraction is unlikely to be 100% complete and total removal of all traces of ungrafted CEL may not, in fact, be realisable practically. Moreover, the calculation[13] assumes the absence of external influences such as simultaneous chain scission.

The molecular weight of the initial ungrafted polymer is higher than that of the ungrafted species. This accords with both the possibility of scission and the likelihood of smaller chains remaining ungrafted.

If there were no scission, the molecular weights would be expected to range in magnitude as (backbone) > (initial polymer) > (ungrafted polymer), which is not borne out by the observed data.

When realistic *LS* errors of ±8% are allowed for the molecular weights of ungrafted and grafted CTC, it is quite feasible for the lower limit of the former and the upper limit of the latter to be 0.56×10^3 and 0.68×10^3 kg/mol, respectively. The initial polymer consists of ~94 wt% material of lower molecular weight which is reduced to $\sim 0.56 \times 10^3$ after scission, and which remains ungrafted. The remaining 6 wt% is material of higher molecular weight which falls to $\sim 0.68 \times 10^3$ kg/mol after scission, and which is grafted. This supposition raises the question as to why the very long backbone falls in molecular weight to a value that is not very markedly greater than that of the scinded ungrafted species. In this connection it is convenient to illustrate the situation in terms of the number-average molecular weights of CEL rather than the weight-average quantities of CTC (the general conclusions are unaltered but, although the conversion of CEL to CTC merely involves a multiplicative factor of 3.20, the factor for the differently averaged molecular weights is constant, but unknown; its value is 2 only if the scission leads to the most probable distribution). Let $(M_n)_0$ (kg/mol) and M_n (kg/mol) denote respectively the number-average molecular weights of initial CEL and the CEL produced after absorption of a dose r (J/kg). If N_a(mol^{-1}) is the Avogadro number and G is the number of scissions per 1.60×10^{17} J absorbed, then it is easily shown that:

$$N_a/M_n = N_a/(M_n)_0 + (6.25 \times 10^{16} rG) \qquad (5)$$

In the present case $r = 1335$ J/kg and an accepted value[14] of 10 may be taken for G in order to estimate from equation (5) the values of M_n for any selected values of $(M_n)_0$. Thus, for $(M_n)_0$ = 125, 250, 500 and 1000 kg/mol, the corresponding molecular weights M_n of degraded polymer are respectively 106, 186, 295 and 419 kg/mol. Hence, when $(M_n)_0$ is large, the absolute difference $[(M_n)_0 - M_n]$ is also large, but when the initial molecular weight is low, there is only a small absolute change in molecular weight after scission. This is consistent with the hypothesis, that the grafted and ungrafted species are initially of high and low molecular weight respectively and that they are degraded to species of not too dissimilar molecular weight.

CONCLUSIONS

The system has the following features: (A) low extent of homopolymerization; (B) graft stable to radiation; (C) easy physical isolation of grafts; (D) backbone unstable to radiation; (E) backbone impossible to isolate physically; (F) very difficult to extract ungrafted substrate completely. The first three points are matters of great convenience. However, the last three are inherent in radiation grafting to CEL and constitute the main reasons why the resultant copolymer is difficult to characterize in a wholly quantitative manner.

In particular, the disparity in values of W_A yielded by duplicate and different types of analysis is suggestive of some physical inhomogeneity in the copolymer sample. The following relation should hold for a copolymer exhibiting compositional heterogeneity[9]:

$$M_C > W_A M_A + W_B M_B \qquad (6)$$

Since, for reasons already stated, it seems preferable to use a molecular weight obtained from a measurement in one mixed solvent to one derived from several single solvents, we may insert a value of $M_C = 1.21 \times 10^3$ kg/mol as the left hand side of equation (6). However, it is found that the equation does not hold and M_C is smaller than the right hand side of the expression. Equation (6) does hold, if a value of 0.735 is taken for W_A which is not very different from the average analytical value of 0.71 used in this work.

The number-average molecular weight of the PS branches was 247 kg/mol, as measured with a Melabs membrane osmometer. It is not possible to calculate the grafting frequency (f) without a knowledge of M_n for the CTC backbone. If the latter is identical with its weight-average value (630 kg/mol), then $f = 0.99$ which must be regarded as the maximum possible value for f. Since M_n for the backbone is more likely to be of the order of ½ (630), a more realistic estimate of f is ~0.50. Grafting frequencies of value less than unity are not without precedent in the literature[15,16] and they preclude a simple backbone/graft model. They are indicative of crosslinking, presence of ungrafted substrate and also, possibly, block copolymer formation. The last two of these seem likely in the present system.

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REFERENCES

1 Guthrie, J. T., Huglin, M. B., and Phillips, G. O. *J. Appl. Polym. Sci.* 1972, **16**, 1017

2 Guthrie, J. T., Huglin, M. B. and Phillips, G. O. *J. Polym. Sci. (C)* 1972, **37**, 205

3 Guthrie, J. T., Huglin, M. B. and Phillips, G. O. *Eur. Polym. J.* 1972, 8, 747

4 Guthrie, J. T., Huglin, M. B. and Phillips, G. O. *J. Appl. Polym. Sci.* 1971, **15**, 1033

5 J. T. Guthrie, Huglin, M. B. and Phillips, G. O. *IUPAC Int. Symp. Macromolecules Helsinki July 1972, Prepr. Vol I Paper II – 26*

6 Guthrie, J. T., Huglin, M. B., Richards, R. W., Shah, V. I. and Simpson, A. H. *Eur. Polym. J.* 1975, **11**, 527

7 Guthrie, J. T., Huglin, M. B. and Phillips, G. O. *Makromol. Chem.* 1971, **149**, 309

8 Johnson, B. L. and Smith, J. in 'Light Scattering from Polymer Solution', (Ed. M. B. Huglin), Academic Press, London–New York, 1972, Ch 2

9 Benoit, H. and Froelich, D. in 'Light Scattering from Polymer Solutions', (Ed. M. B. Huglin), Academic Press, London–New York, 1972, Ch 11

10 Tuzar, Z., Kratochvíl, P. and Straková, *Eur. Polym. J.* 1970, **6**, 1113

11 Strazielle, C. in 'Light Scattering from Polymer Solutions', (Ed. M. B. Huglin), Academic Press, London–New York, 1972, Ch 15

12 Sakurada, I., Ikada, Y. and Nishizaki, Y. *J. Polym. Sci. (C)* 1972, **37**, 265

13 Collins, R., Huglin, M. B. and Richards, R. W. *Eur. Polym. J.* 1975, **11**, 197

14 Chapiro, A., in 'Polymer Handbook', 2nd Edn, (Eds J. Brandrup and E. H. Immergut), Wiley, New York, 1975, p II–482

15 Taga, T. and Inagaki, H. *Angew, Makromol. Chem.* 1973, **33**, 129

16 Hamburger, C. J. *J. Polym. Sci. (A-1)* 1969, **7**, 1023

X-ray diffraction crystallinity measurements on mixtures of polyethylene and atactic polystyrene

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Although X-ray diffraction is used widely for crystallinity measurements on a variety of polymers, particularly polyethylene, less attention has been paid to partly crystalline and partly amorphous composite systems. These may occur as block copolymers, with one type of block being substantially ordered and the other disordered, or as physical mixtures of the two types of polymer. It seems to have been tacitly assumed that the examination of such polymers is straight forward but the purpose of this Note, which reports crystallinity measurements on mixtures of high density polyethylene and atactic polystyrene, is to show that this may not always be the case.

EXPERIMENTAL

The near-linear polyethylene used in the blends was a BP Chemicals Ltd Rigidex experimental grade polymer containing about one butyl branch per thousand carbon atoms. The polystyrene was BP Chemicals Ltd EF grade, an amorphous, atactic polymer having M_w of about 240 000.

Ten mixtures of the two homopolymers, covering the composition range of 100% polyethylene/0% polystyrene to 10% polyethylene/90% polystyrene, in the form of hot pressed sheets, were examined with a Philips powder diffractometer over the 2θ range 14° to 26° using Ni-filtered CuKα radiation. The results were calculated by the method of Matthews, Peiser and Richards[1], as extended by Preedy[2], taking into account also the broad amorphous polystyrene peak at 19.5° 2θ which is almost coincident with the peak from amorphous polyethylene. This then gave the equation:

$$\% \text{ Crystallinity} = \frac{I'_{110} + 1.36I'_{200}}{I'_{110} + 1.36I'_{200} + 0.81A'} \times 100$$

where I'_{110} and I'_{200} are the areas of the (110) and (200) polyethylene reflections and A' is the total area of the amorphous polyethylene and polystyrene broad peak at 19.5° 2θ. From the known compositions of the mixtures and the percentage crystallinity values obtained by the use of the above equation crystallinity values for the polyethylene may be calculated.

RESULTS AND DISCUSSION

The results for the ten mixtures are given in *Table 1*. The crystallinity values in the fourth column should be identical but they increase steadily