

Chapter 3

Radioluminescence in Scintillators in Tritium-labelled Solutions of Polymers

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INTRODUCTION

Progress in the field of tritium detection and continuous improvement in preparation methods for tritium-labelled compounds enables one to use this isotope in the investigation of high molecular weight compounds. The activity of tritium-labelled polymers can be determined as for other organic compounds by combustion of samples and measuring the activity of the tritiated water produced.^{1,2} For insoluble polymers a gel counting method has been developed. In this method the suspension of tritiated polymer in liquid scintillator is counted in the presence of Aerosil[®]. Liquid scintillation counting seems to be the most convenient method for quantitative measurements of radioactive soluble polymers labelled with tritium, because this technique is simple and measurements can be carried out quickly and accurately with the required precision. Tritium is a suitable isotope for labelling organic and biological compounds used as radioactive tracers and indicators because it can easily be incorporated into predetermined molecular structures at specific sites. In the case of macromolecules the range of tritium β -particles is greater than, but comparable with, the geometrical dimensions of polymer molecules. One can therefore expect that for liquid scintillation counting the efficiency of tritium detection will be affected by the macromolecular environment of the radioactive sites. Some additional precautions might thus be necessary when determining the activity of tritiated polymers to ensure the reliability of the scintillation method. The work presented here describes the results of studies on the efficiency of tritium detection in liquid scintillator solutions of polymers when tritium was located either in the polymer, or in the solvent molecules. It has been found that the efficiency of tritium detection for systems of identical composition is dependent only on tritium location. The results obtained are explained in terms of the non-homogeneous distribution of scintillator molecules between solvent and swollen macromolecules of polymer.

EXPERIMENTAL

The liquid scintillation counter USB (Poland) with photomultiplier EMI 9514 S and pulse-height analyser AI-1024 (Soviet Union) were used in our experiments. The optimum parameters for operating counting equipment were as follows: anode voltage 1080 V, discrimination level 0.2 V and amplification 1000 V/V. All measurements were carried out at 0 ± 1 °C at the background level 900 ± 100 cpm. The efficiency of tritium detection was determined using n-hexadecane-1,2-T of known activity supplied by the Radiochemical Centre, Amersham, England. Toluene solutions of various scintillators at concentration 4 g l^{-1} were prepared and the efficiency of tritium detection was found to be equal to 49% for PPO, 46% for α -NPO and 43% for α -NPD.

Table 1. The viscosity-average molecular weight \bar{M}_v for polymers used.

Tritium-labelled polymers		Non-labelled polymers	
Sample	$\bar{M}_v \times 10^{-3}$	Sample	$\bar{M}_v \times 10^{-3}$
PS1-T	241	PS1	241
PS2-T	441		
PS3-T	640		
PS4-T	965	PS4	920
PS5-T	1.200		
PS6-T	1.400		
PMM-T	340	PMM	322

Table 2. The specific activity values for tritium-labelled polymers.

Polymer	Combustion method		Direct dissolving method	
	Sample weight/ mg	Specific activity		Average specific activity $\mu\text{Ci g}^{-1}$
		for sample $\mu\text{Ci g}^{-1}$	average ₁ $\mu\text{Ci g}^{-1}$	
	62	15.28		
	68	15.53		
	97	14.46		
PS1-T	103	15.28	15.06	15.25
	107	15.11	± 0.30	± 0.20
	127	14.73		
	183	15.01		

Tritium-labelled polystyrene (PS-T) was prepared by isotope exchange reaction in dioxane solution between polystyrene, obtained by block polymerization and tritiated water in the presence of HClO_4 . The same operations were carried out with non-labelled polystyrene (PS) used as a blank sample in counting measurements. Tritium-labelled polymethyl methacrylate (PMM-T) was obtained by polymerization of methyl methacrylate in benzene solution in the presence of azobisisobutyronitrile-T as an initiator. Non-labelled polymethyl methacrylate (PMM) was prepared using the same procedure. No differences have been found between labelled and non-labelled polymers as checked by viscosity measurements in benzene solutions at 20 °C. The viscosity-average molecular weights \bar{M}_v of polymers used were calculated according to data of Meyerhoff¹¹ and are shown in Table 1.

The specific activity of tritium labelled polymers was determined by two methods. The first was based on a liquid scintillation technique. The counting rates were

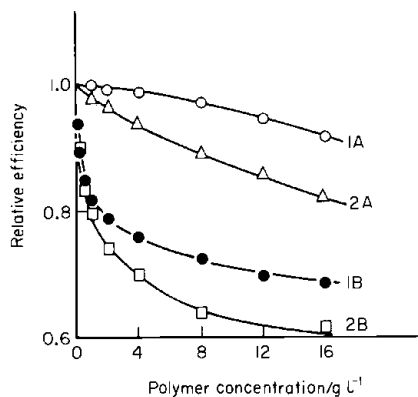


Fig. 1

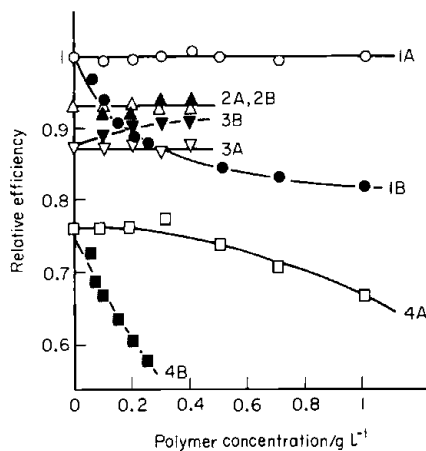


Fig. 2

Fig. 1. The dependence of the relative efficiency of tritium detection on polymer concentration. The concentration of PPO 4 g l^{-1} . 1A, Toluene-T-PS1-PPO; 1B, Toluene-PS1-T-PPO; 2A, Toluene-T-PMM-PPO; 2B, Toluene-PMM-T-PPO.

Fig. 2. The dependence of the relative efficiency of tritium detection on concentration of PS1 (1A/4A) and PS1-T (1B/4B) for concentration of PPO; 1A, 1B - 4 g l^{-1} ; 2A, 2B - 16 g l^{-1} ; 3A, 3B - 20 g l^{-1} ; and 4A, 4B - 0.5 g l^{-1} .

determined in the toluene solution of PPO for various polymer concentrations and the ratios of counting rates to polymer concentrations were extrapolated to infinitely dilute solution. It was assumed that the efficiency of tritium detection for infinitely dilute polymer solution was the same as for solution without polymer. In the second method the polymer samples were burned and the activity of the tritiated water formed was determined. The combustion was carried out in home-made apparatus based on the microanalytical combustion furnace. The results of specific activity determinations for labelled polystyrene obtained by these two methods are in good agreement as shown in Table 2.

RESULTS

The dependence of the detection efficiency for tritium on the polymer concentration has been investigated for the toluene-polymer scintillator systems in which toluene, or polymer was labelled with tritium. The relative efficiency of tritium detection was calculated assuming the efficiency for the standard toluene scintillator (4 g l^{-1}) system equal to 1. The results obtained for the set of PPO solutions are shown in Fig. 1. For the solutions of tritiated polymers (curves 1B and 2B) the efficiency of tritium detection is distinctly lower than in the analogous solution with labelled toluene (curves 1A and 2A). The similar dependence was observed when α -NPO and α -NPD were used as scintillators.

In order to explain such intriguing observations the efficiency of tritium detection for the toluene-polystyrene-PPO system has been investigated as a function of concentration and molecular weight of polymer and concentration of scintillator. Dependence of the relative efficiency on polystyrene concentration for various concentrations of PPO is shown in Fig. 2. For concentrations of PPO up to 16 g l^{-1} the efficiency of tritium detection was always lower when tritium was incorporated in polystyrene molecules (curves 1A, 1B and 4A, 4B). At the concentration of PPO equal to 16 g l^{-1} (curves 2A, 2B) detection efficiency becomes independent of tritium location and polymer concentration. At even higher scintillator concentration equal to 20 g l^{-1} the efficiencies were reversed, being higher for solution of labelled polystyrene (curves 3A, 3B). Figure 3 shows dependence between detection efficiency of tritium and PPO concentration for three systems: toluene-T-PPO, toluene-T-PS1-PPO and toluene-PS-T-PPO. The crossing point of curves 1A and 1B indicates no influence of

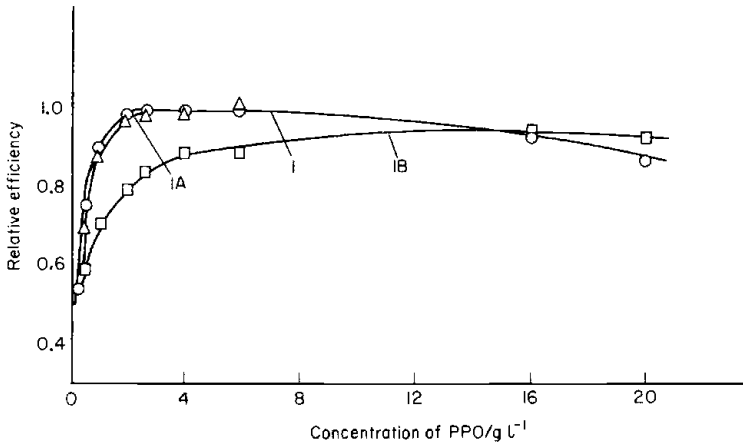


Fig. 3. The dependence of the relative efficiency of tritium detection on concentration of PPO. The concentration of polystyrene 0.25 g l^{-1} , Toluene-T-PPO; 1A, Toluene-T-PS1-PPO; 1B, Toluene-PS1-T-PPO.

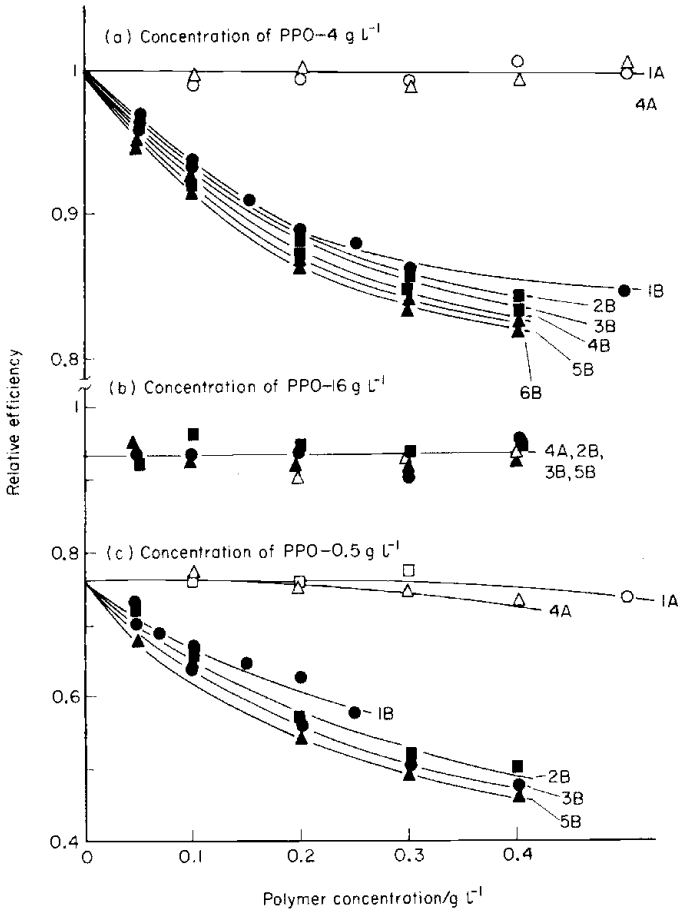


Fig. 4. The dependence of the relative efficiency of tritium detection on concentration of polystyrene of various molecular weights. The concentration of PPO: (a) 4 g l^{-1} ; (b) 16 g l^{-1} ; (c) 0.5 g l^{-1} ; 1A, Toluene-T-PS1-PPO; 4A, Toluene-T-PS2-PPO; 1B/6B, Toluene-PS1/6-T-PPO.

tritium location on efficiency of tritium detection. The relative efficiency of tritium detection as a function of polystyrene concentration for polymer samples with various molecular weights is shown in Fig. 4. Figure 4(a) presents the results for experiments carried out at a constant concentration of PPO equal to 4 g l^{-1} . The efficiency of tritium detection is independent of molecular weight of non-labelled polymer while the influence of molecular weight is clearly seen for tritiated polystyrene. Similar measurements were done for concentrations of PPO equal to 16 g l^{-1} and 0.5 g l^{-1} and results are summarized in Fig. 4(b) and Fig. 4(c). For concentration of PPO 16 g l^{-1} efficiency of tritium detection is constant and independent of concentration and molecular weight of polymers (Fig. 4(b)). Only at a very low concentration of PPO equal to 0.5 g l^{-1} does molecular weight of non-labelled polymer affect the efficiency of tritium detection (curves 1A, 4A in Fig. 4(c)). For tritium-labelled polystyrene at this PPO concentration a considerable decrease of efficiency is observed for polymer samples of growing molecular weights (curves 1B, 2B, 3B, 5B in Fig. 4(c)).

Measurements of scintillation efficiency similar to those presented above were carried out using ^{14}C -isotope as indicator. No differences in scintillation efficiencies have been observed in connection with location of ^{14}C -isotope either in polymer, or in solvent molecules at various compositions of the solutions investigated.

DISCUSSION

The observed effect of the location of radioactive site on tritium detection efficiency is unique for this isotope and due to the low energy and short range of tritium β -particles. When tritium is located in the macromolecule a significant fraction of radioactive disintegration energy will be intercepted in the macromolecule volume. One can assume that conditions for generation of primary excited states of donor molecules in the volume of macromolecules are similar to those in the bulk solvent. This opinion is justified by two facts. Toluene as a good solvent can easily penetrate into the macromolecule volume. Therefore its internal concentration in this volume is very high. It is also known that polymers used in our experiments do not exhibit any observable quenching properties. On the contrary, polystyrene is an efficient donor with regard to the energy transfer processes; therefore it is very often used as a host material in plastic scintillators⁷.

In our opinion the observed effect of tritium location can be explained in terms of the distribution of scintillator molecules between solvent and swollen macromolecules of polymer. In a three-component mixture of toluene, polystyrene and PPO, toluene and PPO might be regarded as a mixed two-component solvent for polystyrene. Due to the different interactions between polymer and solvent components the composition of the solvent should be different inside and outside the macromolecule sphere. PPO is thermodynamically a less favourable solvent for polystyrene than toluene; therefore scintillator molecules will be displaced by toluene molecules from the volume of macromolecules establishing a non-homogeneous distribution of PPO molecules. Concentration of scintillator molecules which act as an energy acceptor and final flow will always be lower in the volume of macromolecules. Such a deficit of scintillator molecules in this volume can be responsible for the decrease of the efficiency of tritium detection for solution with labelled polymer. Enhanced non-radiative decay processes and the growing importance of spontaneous fluorescence of donor molecules occurring at an unfavourable wavelength region can contribute to the lower efficiency observed in our experiments.

The dilute solution of polymer can be regarded as a two-phase system. The swollen macromolecules can be considered as the first phase whereas the molecules of solvent in the outer sphere of macromolecules constitute the second phase. Assuming this quantitative picture of the two-phase system the distribution coefficient of PPO between toluene and polystyrene can be calculated. For concentration of PPO equal to 16 g l^{-1} the efficiency of tritium detection is independent of the tritium location and equal to 0.934 (curves 2A, 2B in Fig. 2). In this case the efficiency of tritium detection in the volume of polystyrene molecules is the same as in bulk solvent. The same efficiency was found in toluene-scintillator solution when concentration of PPO was equal to 1.25 g l^{-1} .

It is thus reasonable to assume that PPO at such concentrations is present in the macromolecular volume. The distribution coefficient K of PPO can now be easily calculated assuming the concentration of scintillator in the solvent outside the macromolecules equal to 16 g l^{-1} . This assumption is justified by very low contribution of macromolecule volume and consequently negligible number of PPO molecules trapped inside polymer molecules. The K value is thus represented by the ratio $16 \text{ g l}^{-1} : 1.25 \text{ g l}^{-1} = 12.8$. As is seen from Fig. 2 and Fig. 4(b) the distribution coefficient value for PPO practically does not depend on molecular weight of polystyrene and its concentration up to 0.4 g l^{-1} . For all the samples the location effect is not observed at a concentration of PPO of 16 g l^{-1} .

In the system with labelled polystyrene and PPO concentration 20 g l^{-1} the efficiency of detection in the volume of macromolecules is higher than in the solvent (curves 3A, 3B in Fig. 3). At such a high concentration of scintillator molecules, an efficient chemical self-quenching process in the bulk solution is occurring which inhibits fluorescence and decreases detection efficiency. In the macromolecule volume self-quenching cannot play any important role because scintillator concentration there is about one order lower.

If assumption of the non-homogeneous distribution of scintillator between swollen macromolecules and the bulk solvent is valid, direct mathematical expression for the dependence between relative efficiency of tritium detection and concentration of labelled polymer should be found. In a solution of toluene-PS-T-PPO there is a great probability that the radioactive decay of tritium takes place in the volume of macromolecule. In this case a significant fraction of β -particle energy is absorbed in the volume of macromolecules. The absolute detection efficiency in liquid scintillator is proportional to the total number of solvent molecules in the excited states which in turn is proportional to the fraction of energy absorbed. Efficiency of detection can now be discussed in terms of energy absorbed inside and outside of macromolecule volume. The absolute detection efficiency of β -particles corresponding to the energy absorbed in the volume of polymer molecules denoted as η_p and the solvent surrounding macromolecules η_s are dependent on the concentration of scintillator and fractions of β -particle energy absorbed in the solvent and polymer phases. The volume of dilute solution of polymer can be expressed as a sum of volumes of macromolecules and surrounding solvent. Detection efficiency in solution should follow the simple additive rule represented by Eqn (1).

$$\eta = \eta_s \varphi_s + \eta_p \varphi_p \quad (1)$$

$$\varphi_s + \varphi_p = 1 \quad (2)$$

where η = absolute efficiency of tritium detection in solution with labelled polymer, φ_p = volume fraction of swollen macromolecules and φ_s = volume fraction of solvent. In Eqn (1) and Eqn (2) the volume fraction of scintillator has not been included because in solutions used its contribution is negligible. Dividing Eqn (1) by absolute efficiency of tritium detection η_0 in standard solution i.e. toluene + PPO (4 g l^{-1}) we obtain Eqn (3) for relative efficiencies:

$$\frac{\eta}{\eta_0} = \frac{\eta_s}{\eta_0} \varphi_s + \frac{\eta_p}{\eta_0} \varphi_p \quad (3)$$

The ratios η/η_0 , η_s/η_0 and η_p/η_0 express the relative efficiencies and are further written as \underline{E} , \underline{E}_s and \underline{E}_p respectively. Substituting (2) into (3) one obtains Eqn (4).

$$\underline{E} = \underline{E}_s - (\underline{E}_s - \underline{E}_p) \varphi_p \quad (4)$$

Since the radius of macromolecules is far smaller than the average range of tritium β -particles it can be assumed that the absolute efficiency η_s in the solvent outside macromolecules is close to the efficiency in the bulk solution. The volume fraction of polymer φ_p can be expressed as:

$$\varphi_p = \frac{AV}{\underline{M}} \quad (5)$$

Table 3. The values of macromolecule volume \bar{V}_p calculated from the scintillation measurements.

Polymer sample	PS1-T	PS2-T	PS3-T	PS5-T
$\bar{V}_p \times 10^{-8}$ \AA^3	4.1	9.2	15.3	32.0

where \underline{c} = concentration of polymer (g l^{-1}), \bar{V}_p = average volume of macromolecule (1), \bar{M} = number-average molecular weight of polymer, and A = Avogadro's number. Combining Eqn (4) and Eqn (5) linear expression which presents dependence between relative efficiency \underline{E} and concentration of polymer \underline{c} is obtained

$$\underline{E} = \underline{E}_s - (\underline{E}_s - \underline{E}_p) \frac{AV}{\bar{M}} \underline{c} \quad (6)$$

Experimentally determined relations between \underline{E} and \underline{c} are approximately linear for small concentrations of polystyrene at various concentrations of PPO. This confirms the validity of the assumptions made. Deviation from the linear relation of PS-T greater than 0.2 g l^{-1} can be caused by interactions between neighbouring macromolecules, which in turn can affect values of \underline{E}_s , \underline{E}_p and \bar{V}_p .

Taking into consideration the distribution coefficient of PPO calculated previously the concentration of PPO in the volume of macromolecules can easily be found. For the solution of total concentration of PPO, $\underline{c} = 0.5 \text{ g l}^{-1}$, the concentration in the volume of macromolecules equals $\underline{c}/K = 0.039 \text{ g l}^{-1}$. At such low 'internal' concentration of PPO in the volume of macromolecules combined with relatively small absorption of β -particle energy occurring in this volume, the efficiency \underline{E}_p in this case is near zero. With this approximation the slope of line given by Eqn (6) is equal to $\underline{E}_s AV / \bar{M}$ and $\underline{E}_s = 0.76$. These data allow us to find the volumes of macromolecules \bar{V}_p from the slopes of linear dependence between the relative efficiency of tritium detection and concentration of labelled polystyrene of different molecular weights. Calculated values \bar{V}_p are presented in Table 3. In calculations of \bar{V}_p volumes the viscosity-average molecular weights were used.

In order to compare the \bar{V}_p values found the approximate macromolecule volumes have been calculated using another method. Assuming the globular shape of macromolecules in solution and taking diameters \underline{d} of these globules as the distance between the most remote segments of polymer chain, the value \underline{d} can be calculated from Eqn (7).

$$\underline{d} = 1.4(\overline{h^2})^{1/2} \quad (7)$$

where $\overline{h^2}$ is the quadratic mean distance between the ends of the polymer chain. The volume of macromolecule \underline{V} is represented by Eqn (8).

$$\underline{V} = 1.432(\overline{h^2})^{3/2} \quad (8)$$

For calculations of $(\overline{h^2})^{3/2}$ the intrinsic viscosities corresponding to infinitely diluted toluene solution of polystyrene at 0°C and average experimental value of Flory constant $\Phi = 2.1 \times 10^{21}$ have been used. The calculations were carried out using Eqn (9).

$$\frac{(\overline{h^2})^{3/2}}{\Phi} = \frac{(\eta) \underline{M}}{\Phi} \quad (9)$$

Taking into consideration (8) and (9) the average values of volume of macromolecule \underline{V} were obtained and are shown in Table 4.

Table 4. The intrinsic viscosities in infinitely diluted toluene solution of polystyrene(η) at 0 °C and values of macromolecule volume \underline{V} calculated from viscosity measurements.

Polymer sample	PS1-T	PS2-T	PS3-T	PS5-T
(η)	0.87	1.48	2.00	3.23
$\underline{V} \times 10^{-8}$	1.4	4.4	8.7	26.5
ρ^3				

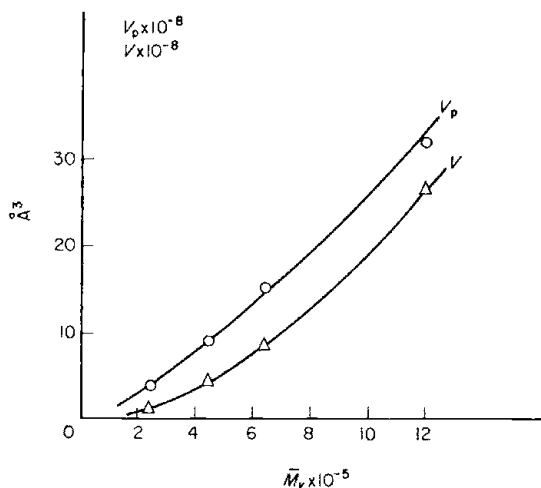


Fig. 5. The dependence of the calculated volumes of macromolecule on the molecular weight of polystyrene.

The calculated volumes \underline{V} and \underline{V}_p are compared in Fig. 5 when plotted against the molecular weight of polymer. One should not expect good agreement of \underline{V} and \underline{V}_p values because of their different physical sense and different assumptions taken for calculations. The similar shape of curves in Fig. 5 indirectly confirms the validity of the hypothesis on non-uniform distribution of scintillator molecules in a liquid solution of polymers.

SUMMARY

The relative efficiency of tritium detection was determined in the solvent-polymer scintillator system in which the solvent, or polymer was labelled with tritium. It has been found that the efficiency of detection is dependent on tritium location being lower when tritium was located in the polymer molecules. The above mentioned effect has been observed in toluene solutions of polystyrene (PS), polymethyl methacrylate (PMM) in the presence of such scintillators as: PPO, α -NPO and α -NPD. Dependence of detection efficiency of tritium on concentration and molecular weight of polymer and concentration of scintillator was investigated for the toluene-PS-PPO system.

The results obtained have been explained in terms of the distribution of the scintillator molecules between solvent and swollen macromolecules of polymer. From our results the distribution coefficient of PPO between toluene and PS has been calculated and found equal to 12.8. For dilute solutions of PS the volume of macromolecule has been calculated and compared with data obtained from viscosity measurements.

It seems that specific activity of tritiated polymers can be accurately determined by the method based on direct dissolving of labelled polymer in the liquid scintillator. It was assumed, however, that the efficiency of tritium detection for infinitely dilute polymer solution was the same as for solution without polymer. The specific activity values obtained in this way are comparable with those obtained by the combustion method.

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REFERENCES

1. J. Car and B.E. Gordon, J. Polymer Sci. C8, 71 (1965).
2. J.Y. Yang, J. Polymer Sci. B4, 31 (1966).
3. W. Hoffmann, Radiochim. Acta 1, 216 (1963).
4. G. Meyerhoff, Z. Phys. Chem. 4, 338 (1955).
5. G. Schulz and G. Meyerhoff, Z. Electrochem. 56, 904 (1952).
6. P. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, 1953.
7. S. Sandler, Nucleonics 18, 102 (1960).
8. W. Kuhn, Experimentia 1, 28 (1945).

DISCUSSION

G.W.A. NEWTON: The loss in efficiency was due to PPO adsorbed in the PS polymer. Why was there no loss due to toluene-T in the polymer? Why bother with PPO adsorption? Isn't the effect of increasing M on the PS-T due to decrease in surface to volume ratio?

J. GEBICKI: Toluene as a good solvent for polystyrene can easily penetrate into macromolecule volume and its internal concentration in this volume is very high. Therefore we could approximately assume that toluene molecules are uniformly distributed in all solutions. The macromolecules of polystyrene filled with toluene molecules can be considered as a separate microphase. The changes in efficiency of tritium detection in the system investigated have been explained in terms of distribution of scintillator molecules between such a microphase of polymer and a phase of solvent surrounded macromolecules.