Synthesis, characterization and photophysical properties of benzil-labelled polymers for studies of diffusion-limited interactions by phosphorescence quenching

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A new technique for synthesizing benzil-labelled polystyrenes has been developed. This new procedure has advantages over an older synthesis by Horie and Mita in that it involves fewer and less complicated synthetic steps. In addition, the new synthetic pathway should allow for labelling of different sites on the polymer chain and for labelling of different polymers such as poly(methyl methacrylate). The phosphorescence lifetime of terminally benzil-labelled polystyrenes in cyclohexane was found to be approximately 85–90 μs at 25°C with the concentration of benzil at 10^{-5} M and was independent of labelled polystyrene molecular weight and polystyrene concentration up to $150 \, g \, l^{-1}$. When used in phosphorescence quenching studies, these materials were found to exhibit non-single-exponential lifetimes in the presence of anthracene and azulene quenchers for a concentration of benzil label $\leqslant 10^{-4}$ M. An explanation for this anomalous behaviour and a technique for decoupling these decays into two lifetimes has been proposed. This technique should allow for the study of diffusion-limited interactions occurring in higher-molecular-weight polymer systems where the label concentration $\leqslant 10^{-4}$ M.

(Keywords: phosphorescence quenching; diffusion; end-labelled polystyrene; anionic polymerization; phosphorescence lifetime)

INTRODUCTION

The synthesis of functionalized polymers bearing photophysical labels has received a great deal of attention in recent years. Winnik et al.[1] have synthesized pyrene end-capped polystyrenes for studies of cyclization dynamics. Later, Tang et al.[2] synthesized pyrene end-labelled polystyrene having no ester linkages, giving the material enhanced thermal stability. It is also possible to end-label the same chain with two different labels. Slomkowski and Winnik[3] have recently synthesized polytetrahydrofuran with benzil on one chain end and pyrene on the other chain end for further cyclization studies. Labelling polymers at sites other than the chain end has also been done. Tran-Cong et al.[4] have randomly labelled polystyrene with the photodimerizable probe bis(9-anthrylmethyl) ether for use in diffusion experiments using forced Rayleigh scattering (FRS). Wesson et al.[5] have synthesized azobenzene end- and centre-labelled polystyrenes for use in FRS self-diffusion studies. Deschamps et al.[6] have synthesized spiropyran end-labelled polystyrenes for FRS self-diffusion measurements at the theta temperature. Very recently, copolyesters containing photolabile units in the main chain have been synthesized[7]. The labelling of polymers with functional groups is important not only because it allows for the study of basic polymer physics such as diffusion but also because many of these labelled polymers are industrially important. Some recent applications of functionalized polymers include macromolecular catalysts, polymers having energy-converting capabilities and photoresponsive membranes[8].

A powerful technique for the study of diffusion-limited interactions in polymer systems is phosphorescence quenching[9–12]. One advantage that phosphorescence quenching has over other photophysical techniques such as fluorescence quenching is the very long lifetimes of phosphorescence probes, which extend the dynamic range of experiments by several orders of magnitude. This fact is particularly important when performing studies in highly entangled polymer systems, where the mobility of the polymer molecules is expected to be significantly reduced. Horie and Mita have successfully covalently attached the phosphorescence moiety benzil onto the chain end of polystyrene[9] and have used phosphorescence quenching as a model to perform an important study on polymer chain-end interactions[11]. Their procedure involves three synthesis steps: termination of 'living' polystyrene with carbon dioxide, conversion of the carboxylic acid-terminated polystyrene into an acid chloride-terminated polystyrene by reaction with thionyl chloride, and, finally, reaction of the acid chloride-terminated polystyrene with 4-hydroxymethylbenzil to form benzil-terminated polystyrene. A critical step in this synthesis is separation of the unreacted thionyl chloride from the acid chloride-terminated polystyrene. This procedure is very time-consuming, and as a result there was a strong motivation to modify the synthesis.

One of the most direct methods of producing functionalized polymers is to terminate the living polymer

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with a halogenated form of the label. For example, anthracene-labelled polystyrenes have been successfully synthesized by terminating living polystyrene with 9-chloromethylanthracene[9,13]. This technique cannot be applied to carbonyl-containing labels such as 4-bromomethylbenzil, as the carbonyl groups are subject to nucleophilic attack by the living polymer anion. To overcome this problem, the carbonyl group must be 'protected'. A common technique is to lower the reactivity of the anion by reaction with 1,1-diphenylethylene[14,15]. This will sterically hinder the living carbanion and sufficiently lower its reactivity so that reaction with the carbonyl group is unfavourable. This method has been successfully applied to anionic polymerization of carbonyl-containing monomers such as methyl methacrylate[15,16]. It is this technique that was used for protecting 4-bromomethylbenzil.

EXPERIMENTAL

Synthesis of 4-bromomethylbenzil

The synthesis of 4-bromomethylbenzil was carried out as described by Horie and Mita[9]. The synthetic sequence that they used is shown in *Figure 1*. 4-Methyldeoxybenzoin was prepared according to the procedure of Bavin[17]. To 100 g of phenylacetyl chloride (Aldrich) is added 100 g of anhydrous aluminium chloride (Aldrich) and 690 ml of toluene. The mixture is refluxed for 1 h and a system for absorbing hydrogen chloride is provided. The mixture will turn from clear to green to black. If at the start of the reaction the phenylacetyl chloride is not perfectly clear, an undesirable by-product with a very strong odour will result from this reaction. After 1 h the reaction mixture is poured onto a mixture of 650 g ice and 260 g concentrated HCl to quench the reaction. The aqueous phase is extracted once with toluene. The organic phase containing 4-methyldeoxybenzoin in toluene is dried with sodium carbonate, and the toluene is evaporated using a rotary evaporator. The remaining solid 4-methyldeoxybenzoin is recrystallized from methyl alcohol and has a melting point of 100°C. The yield of 4-methyldeoxybenzoin from this reaction is about 90%.
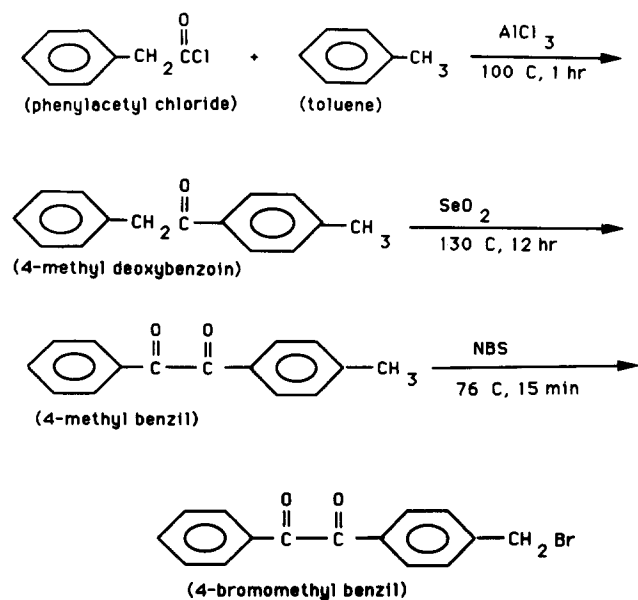

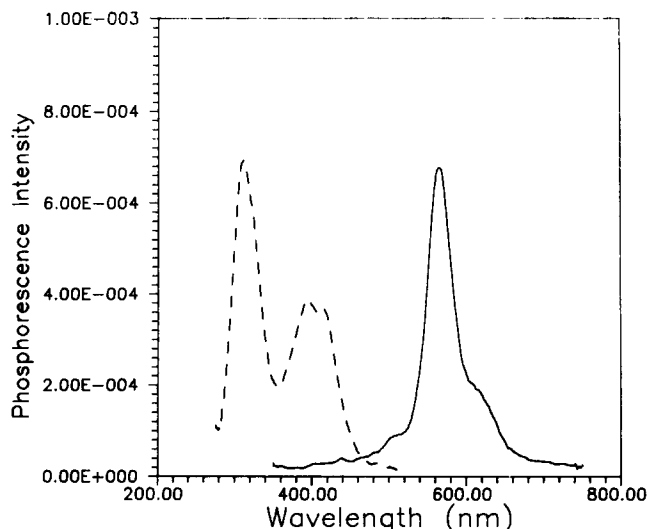**Figure 1** Synthetic route to 4-bromomethylbenzil

Figure 2 Room-temperature phosphorescence spectrum of 1×10^{-3} M 4-methylbenzil in cyclohexane at 50 μs delay time: (— — —) excitation spectrum, $\lambda_{em} = 560$ nm; (——) emission spectrum, $\lambda_{ex} = 300$ nm

The 4-methyldeoxybenzoin is oxidized to 4-methylbenzil according to the procedure of Corey and Schaefer[18]. A mixture of 12.3 g 4-methyldeoxybenzoin, 15.5 g selenium oxide, 105 ml glacial acetic acid and 45 ml water is refluxed for 12 h. Then 200 ml of water is added to quench the reaction. The reactor contents containing the 4-methylbenzil product are extracted twice with ethyl ether. Sodium carbonate is added to the ether phase containing the 4-methylbenzil to neutralize the acid. This neutralization will release large quantities of carbon dioxide gas, so it must be done very slowly to avoid loss of product. At this point the ether phase should be bright yellow. The ether phase is filtered and the ether is evaporated away, leaving a viscous, intense yellow oil of 4-methylbenzil. The phosphorescence emission spectrum of 4-methylbenzil in cyclohexane at 25°C is shown in *Figure 2*. The lifetime of 1×10^{-3} M 4-methylbenzil in cyclohexane at 25°C is approximately 35 μs.

The 4-methylbenzil is converted to 4-bromomethylbenzil according to the method of Krieg and Manecke[19]. To 7 g of 4-methylbenzil are added 10 ml carbon tetrachloride, 8.4 g N-bromosuccinimide and 1 g benzoyl peroxide. The reaction mixture is refluxed for 15 min. The product is recrystallized from n-pentane at 0°C and results in yellow needles that have a melting point of 69°C. The phosphorescence emission spectrum of 4-bromomethylbenzil is shown in *Figure 3*. The phosphorescence lifetime of 1×10^{-3} M 4-bromomethylbenzil is 24 μs in cyclohexane at 25°C. The structure of 4-bromomethylbenzil was verified by both n.m.r. spectroscopy and mass spectrometry. N.m.r. measurements were done on a 90 MHz Varian EM-390 instrument. The n.m.r. chemical shifts are 4.5, 7.5–7.6 and 7.9–8.0 ppm from tetramethylsilane (TMS), with intensity ratios of 2:5:4 corresponding to aliphatic protons, monosubstituted phenyl protons and disubstituted phenyl protons, respectively. Mass spectrometry measurements were done on a HP 5985B GC/MS instrument. Peaks for M/Z were observed at 302, 303 and 304, and at 223 corresponding to 4-bromomethylbenzil (with three isotopes of bromine) and 4-methylbenzil, respectively.
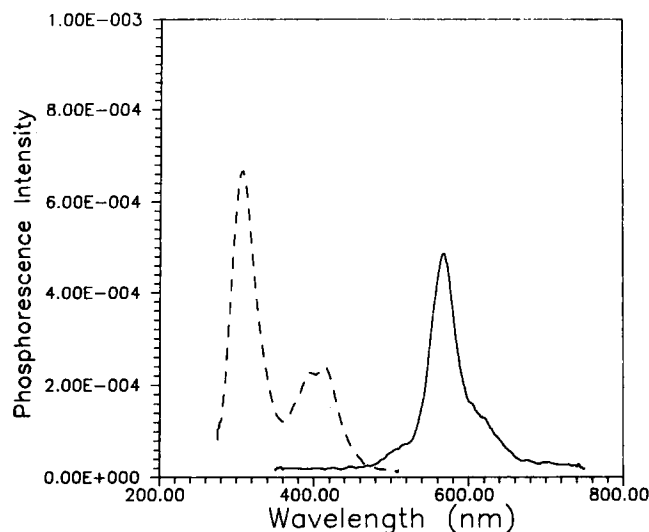
Figure 3 Room-temperature phosphorescence spectrum of 1×10^{-3} M 4-bromomethylbenzil in cyclohexane at $50\,\mu s$ delay time: (————) excitation spectrum, $\lambda_{em} = 560$ nm; (———) emission spectrum, $\lambda_{ex} = 300$ nm

Synthesis of benzil-terminated polystyrene

The synthesis of benzil-terminated polystyrene requires two consecutive reactions onto 'living' polystyrene. Living polystyrene is prepared by the method of anionic polymerization under an inert atmosphere of nitrogen. The techniques employed in this polymerization are similar to techniques used by others who have prepared living polymers under an inert-gas atmosphere[20-23]. The solvent used in the polymerization (cyclohexane, tetrahydrofuran (THF) or benzene) is purified by refluxing over liquid sodium–potassium alloy for several days prior to use and is introduced into the reaction vessel under nitrogen. The oxygen-containing impurities can be removed more rapidly by adding a small amount of benzophenone $(0.01\,g\,l^{-1})$ to the refluxing solvent. Benzophenone will form a ketal radical in the presence of sodium, which will appear blue at first and then purple, indicating that oxygen and water have been scavenged from the system. Note that if too much benzophenone is added to the solvent or if the solvent contains too much water when the benzophenone is added, benzophenone and other by-products may distil off with the solvent, introducing undesirable impurities into the solvent. When using THF as a solvent, it is imperative that the polymerization be carried out at a temperature lower than $-35°C$, since at higher temperatures THF can undergo a ring-opening reaction in the presence of n-butyllithium[24].

Inhibitor is removed from the styrene monomer (Aldrich) by stirring for 8 h with approximately 1 g of 4-tert-butylcatechol remover (Aldrich) per 100 ml of monomer. Also 1 g of calcium hydride (Aldrich) per 100 ml of monomer is added to remove any water that might be present in the monomer. Monomer is then filtered and bubbled with high-purity nitrogen gas (Linde) for 30 min prior to syringe injection into the main reactor. For higher-molecular-weight syntheses, 0.5 ml of 1 M dibutylmagnesium (Alfa) is added to 50 ml of styrene monomer and stirred with a glass stirrer until the styrene turns yellow. At this point the styrene should be water-free and is vacuum distilled with nitrogen gas directly into the reactor. The final concentration of styrene in the reactor is between 10 and $50\,g\,l^{-1}$. At higher

monomer concentrations, the reactions are performed in benzene or cyclohexane at 50°C to avoid the possibility of phase separation, which could interfere with the molecular-weight distribution of the polymer formed.

Initiation is performed at room temperature with injection of 1.3 M s-butyllithium in cyclohexane (Aldrich). Successful polymerization is indicated by a red–orange colour due to the presence of the polystyryl anion. Living polystyrene is transferred to a vessel containing a five times molar excess of 1,1-diphenylethylene to polystyryl anion to form living polystyrene with a reduced reactivity. The 1,1-diphenylethylene is purified prior to this addition by putting it under vacuum and then filling with purified nitrogen gas several times in order to deoxygenate this material. The polystyryl anion will slowly change from red–orange to cranberry coloured over a period of two days, indicating the presence of the diphenyl anion. This material is then transferred to another vessel containing 4-bromomethylbenzil in two times molar excess relative to the carbanion. The 4-bromomethylbenzil is purified by heating at 100°C for 2 h followed by putting the material under vacuum and back-filling with nitrogen several times prior to addition of the living polymer. The solution will slowly turn from cranberry coloured to yellow as the benzil-terminated polystyrene forms. Typically, this reaction requires several days to reach completion at 25°C.

Measurement of phosphorescence lifetimes and quenching rate-constant determination

All phosphorescence emission measurements are performed on a SPEX phosphorimeter using either right-angle or front-face geometry with an excitation wavelength of 300 nm and an emission wavelength of 560 nm. Other phosphorimeter parameters include the following: delay time, $10-250\,\mu s$; window, $40\,\mu s$; and number of flashes per data point, 999. Corrections for variations in xenon lamp intensity due to wavelength, voltage and lamp age are automatically performed by the phosphorimeter through the use of a reference intensity.

For the case of polymer–polymer quenching experiments, a series of five solutions are prepared containing benzil-labelled polystyrene, anthracene-labelled polystyrene and unlabelled polystyrene. The concentration of benzil is the same in all five solutions. A different quantity of both quencher (anthracene-labelled polystyrene) and matrix (unlabelled polystyrene) is added to each solution such that the overall concentration of both labelled and unlabelled polystyrene remains constant in all five samples. The concentration of quencher is kept between 0 and 4×10^{-5} M. All solutions are degassed by performing seven freeze–pump–thaw cycles.

To measure the phosphorescence lifetime for a given solution, the signal intensity is measured with a pulsed Xenon light source at 10 or more decay times to form a decay curve. In the case of a single-exponential lifetime decay, the lifetime is determined from the following relationship:

$$I(t) = I(t=0)\exp(-t/\tau) \qquad (1)$$

where $I(t)$ is the intensity at time t and τ is the phosphorescence lifetime. In some cases the decay may not be single-exponential and a more sophisticated analysis is required to obtain a lifetime. More details on the cause of this non-single-exponential behaviour and

a technique for decoupling such a decay curve are provided later in this paper.

To obtain a quenching rate constant, k_q, the reciprocal lifetime is plotted as a function of quencher concentration to yield a straight line according to the Stern–Volmer equation:

$$1/\tau = 1/\tau_0 + k_q[Q] \tag{2}$$

where τ_0 is the phosphorescence lifetime in the absence of quencher and τ is the phosphorescence lifetime in the presence of quencher at a concentration [Q]. The error in k_q is determined by computing the standard deviation via the Student t distribution at the 80% confidence level.

CHARACTERIZATION

Purification of benzil-labelled polystyrene

Benzil-labelled polystyrene is purified of unreacted 4-bromomethylbenzil by precipitating in methanol and then extracting with hot methanol in a Soxhlet extractor for several days. It is important that the precipitated polystyrene be in a powdery form so that the methanol can contact all of the labelled polystyrene. It is also important to check that all small molecule contaminant has indeed been removed by reprecipitating the polymer once more into methanol and determining that the effective concentration of label has not changed.

Molecular-weight determination

The molecular weight of the anionically synthesized polystyrene is determined by both intrinsic viscosity measurements[25] in cyclohexane at 34.5°C and gel permeation chromatography measurements[26]. A comparison of the molecular-weight averages for benzil-terminated polystyrene synthesized with and without the use of end-capping with 1,1-diphenylethylene is provided in *Table 1*. The polymers in *Table 1* were produced with identical monomer-to-initiator ratios. Therefore, the higher molecular-weight averages and broader molecular-weight distribution for the polymer produced without the use of 1,1-diphenylethylene may be associated with partial coupling of the living polystyrene during the termination reaction. (This will be discussed in more depth later in the paper.)

Determination of labelling efficiency

Since the concentration of labelled polymer is an important parameter for most diffusion experiments, it is important to determine the fraction of polystyrene that is labelled. For labels that absorb light strongly in the ultra-violet or visible spectrum, such as anthracene, this task is fairly straightforward. The absorbance spectrum of the labelled polymer is measured, and the label concentration is determined from the molar extinction coefficient of the label at a wavelength where the polymer does not significantly absorb light. This technique assumes that the labelled probe has the same extinction coefficient as the unlabelled probe. Unfortunately, this technique cannot be used successfully with benzil-labelled polystyrene since the absorbance spectrum of benzil overlaps that of polystyrene. Other techniques such as n.m.r. or i.r. spectroscopy will also not work since the label concentration relative to polystyrene is usually too small.
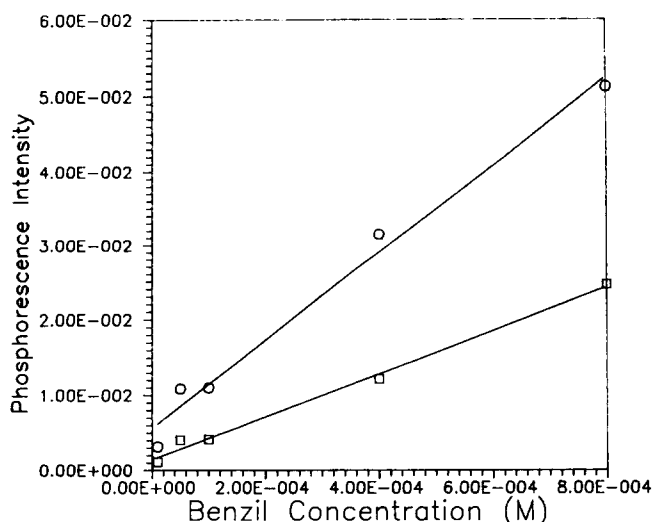

Figure 4 Phosphorescence emission intensity of benzil as a function of benzil concentration in cyclohexane: (○) 50 μs delay time; (□) 100 μs delay time

Table 1 Polymer characterization data

Sample	M_v	M_n	M_w	M_w/M_n	Labelling
PS-X-B[a]	13 900	12 700	14 200	1.12	0.13
PS-B[b]	18 800	18 700	24 600	1.31	–

[a] 1,1-Diphenylethylene end-capped
[b] Polymerization done identically as with sample PS-X-B except that no 1,1-diphenylethylene was used for end-capping the living polystyrene prior to termination

Phosphorescence has been used to determine concentrations of molecules in solutions where other techniques fail, and has been shown to be a very sensitive technique, especially at low chromophore concentrations[27]. It is known that a correlation between the phosphorescence emission intensity and the molar concentration of chromophore exists. This correlation is linear if the concentration of chromophore is very low[28]. Indeed, this turns out to be the case for benzil at concentrations less than 10^{-3} M, as is shown in *Figure 4*. Here the phosphorescence intensity of benzil is shown as a function of benzil concentration in cyclohexane.

A known quantity of unlabelled polystyrene was added to the solutions to correct for any static quenching effects[10]. To determine label content on the labelled polystyrenes, this same quantity of labelled polystyrene was added to the appropriate solvent and the phosphorescence emission intensity was measured and compared with the intensity on the calibration curve in *Figure 4*.

RESULTS AND DISCUSSION

Comparison of synthetic techniques

Horie and Mita's synthesis of benzil-terminated polystyrene is shown in *Figure 5*. It involves three reactions with the living polystyrene. In contrast, the new synthesis procedure, as is shown in *Figure 6*, involves only two reactions with living polystyrene and involves no complicated separations. The extension of this technique to
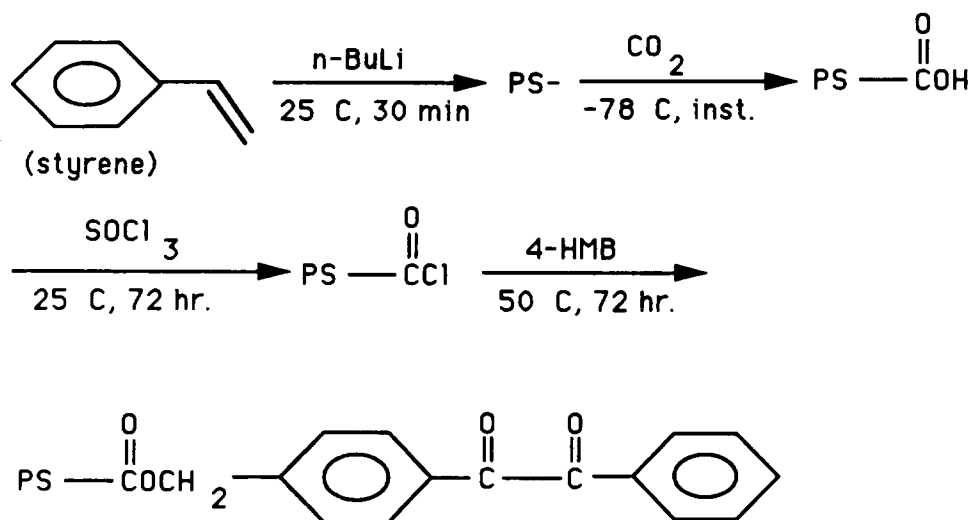
Figure 5 Synthetic route to benzil end-labelled polystyrene, from Horie and Mita[9]
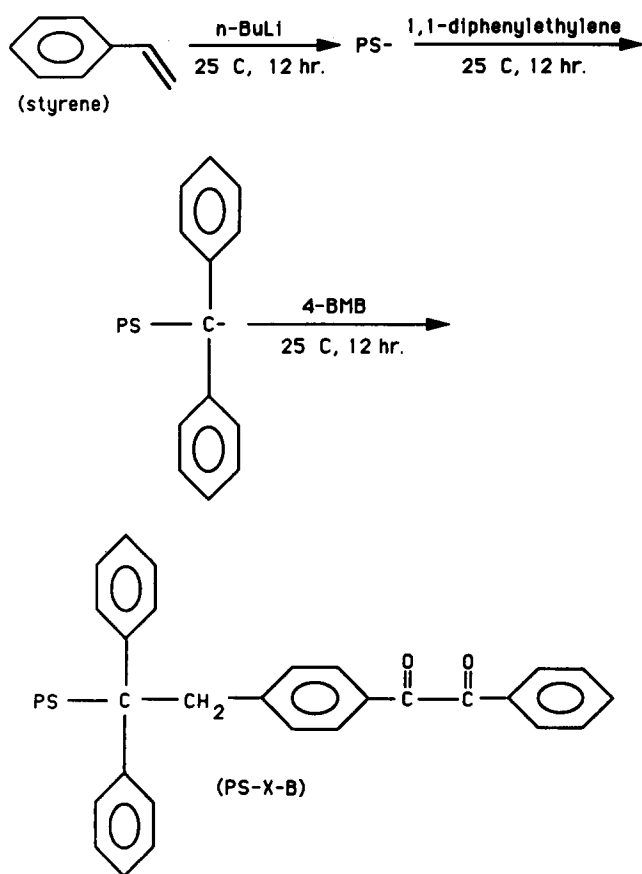

Figure 6 New synthetic route to benzil end-labelled polystyrene (PS-X-B)

Figure 7 (a) G.p.c. trace of 18 000 PS-B synthesized without 1,1-diphenylethylene, indicating bimodal molecular-weight distribution. (b) G.p.c. trace of 13 900 PS-X-B synthesized with 1,1-diphenylethylene

labelling other polymers such as poly(methyl methacrylate) is very simple, since this particular polymerization also requires the use of 1,1-diphenylethylene to protect the carbonyl group of methyl methacrylate.

When reaction of living polystyrene is performed with 4-bromomethylbenzil, a phosphorescing polymer results. However, the polymer has a bimodal molecular-weight distribution, as is shown in *Figure 7a*. (The molecular-weight characterization of the resulting polymer, PS-B, is given in *Table 1*.) It is hypothesized that this is the result of a coupling reaction between the
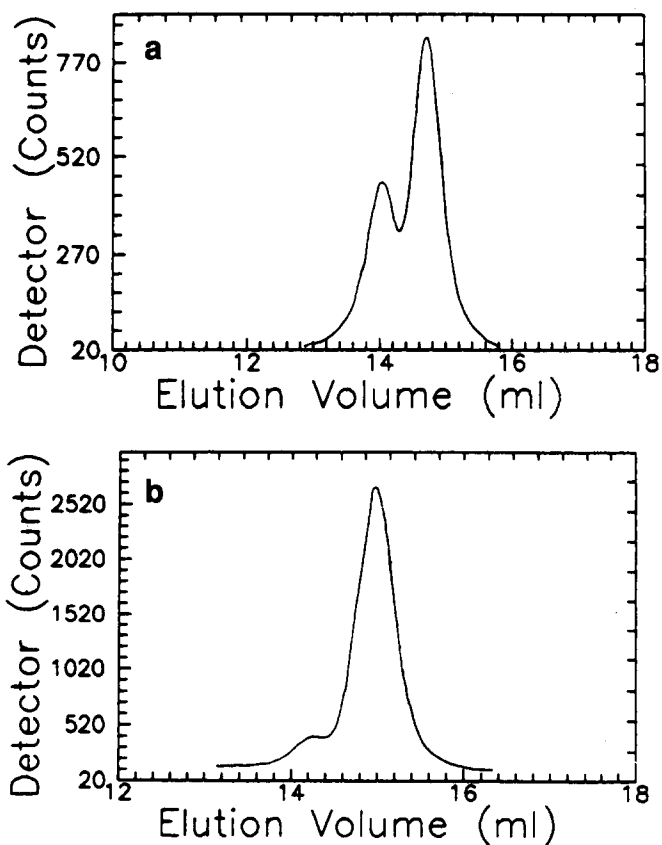
living polystyrene and one of the carbonyl groups in the 4-bromomethylbenzil molecule. Another possible explanation for this bimodal distribution is metal–halogen interchange[2] between the living polystyrene and the halogenated terminator. In either case, this results in a mixture of benzil-labelled polystyrene of two molecular weights, the higher one being twice the molecular weight of the lower one.

To prevent coupling from occurring, 1,1-diphenylethylene is reacted with the living polystyrene to sterically hinder the carbanion and thus only allow it to react with
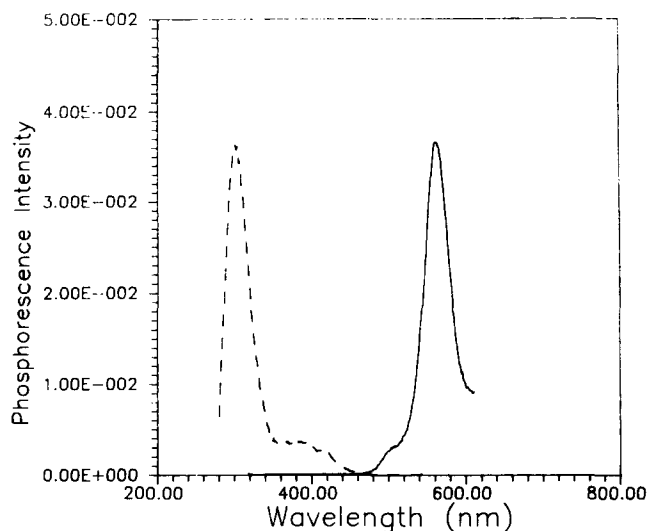
Figure 8 Room-temperature phosphorescence spectrum of $20 \, gl^{-1}$ 13900 PS-X-B (13% labelled) in cyclohexane at $50 \, \mu s$ delay time: (----) excitation spectrum, $\lambda_{em} = 560 \, nm$; (——) emission spectrum, $\lambda_{ex} = 300 \, nm$

the more reactive bromomethyl group on the 4-bromo-methylbenzil terminator. When this is done, a phos-phorescing, nearly monodisperse benzil-labelled poly-styrene results. The narrow molecular-weight distribution of this polymer is indicated by the g.p.c. trace in *Figure 7b*. (The molecular-weight averages of the polymer produced in this manner, PS-X-B, are given in *Table 1*.) Its phosphorescence emission spectrum is shown in *Figure 8*. It should be noted that PS-B (g.p.c. trace shown in *Figure 7a*) and PS-X-B (g.p.c. trace shown in *Figure 7b*) had identical synthesis histories (ratio of monomer to initiator, solvent, etc.) until the end-capping and termination were performed. Thus, the use of 1,1-diphenylethylene in end-capping the living polystyrene is clearly important in this procedure in order to produce nearly monodisperse polymer. It is conceivable that the reactivity of the living polystyrene could also be lowered by reducing the temperature of the reaction to $-77°C$ with the use of a dry-ice/acetone bath. This procedure would require the use of a solvent such as THF, since both benzene and cyclohexane freeze at $6°C$. In addition, it would require providing a means of cooling both the reactors and the transfer needles, and consequently is less convenient than the reaction with 1,1-diphenylethylene.

Lifetime dependence of benzil-terminated polystyrene on inert polystyrene concentration and benzil-terminated polystyrene molecular weight

The dependence of small-molecule benzil lifetime and intensity on polystyrene concentration was investigated in a variety of solvents by Horie and Mita[29] and later by Yu and Torkelson[30]. The results on benzil/polystyrene/cyclohexane solutions studied by Yu and Torkelson are shown in *Figure 9*. It can be seen that at low polymer concentration the lifetime decreases sharply with in-creasing polymer concentration but then levels off to a constant value at higher polymer concentrations. A qualitative explanation for this behaviour is that the reduction in benzil lifetime with polystyrene addition is due to quenching of the benzil molecule by an 'impurity' bound to the polystyrene molecule[29,30]. Furthermore, for the systems studied, the region in which the lifetimes

exhibit a plateau is always semidilute, where there is polymer coil overlap.

The dependence of the phosphorescence lifetime of benzil-terminated polystyrene on inert polystyrene mol-ecular weight in cyclohexane is shown in *Figure 9* as well. The lifetime is approximately $85 \, \mu s$ over the whole inert polymer concentration range from 20 to $150 \, gl^{-1}$. It is also interesting to note that this lifetime is approximately equal to the lifetime of small-molecule benzil in cyclo-hexane at high inert polymer concentrations[30]. This implies that even in dilute solution the benzil label on the polymer chain end is always in a local environment of impurity quencher that is similar to that of a benzil molecule dispersed in a concentrated polymer solution.

The relationship between the benzil-terminated poly-styrene phosphorescence lifetime τ and polystyrene molecular weight is shown in *Table 2*. It has been found that there is virtually no dependence of benzil lifetime on polymer molecular weight for the samples tested in this study. This is in contrast to results of Horie and Mita[9], who reported significantly different lifetimes for their different molecular-weight benzil-terminated systems. They attributed their lifetime differences to differing levels of impurities that were incorporated into the polymer chain during their synthesis. Also reported in *Table 2* is the percentage benzil labelling of the polymer samples. While the samples employed in this study had benzil
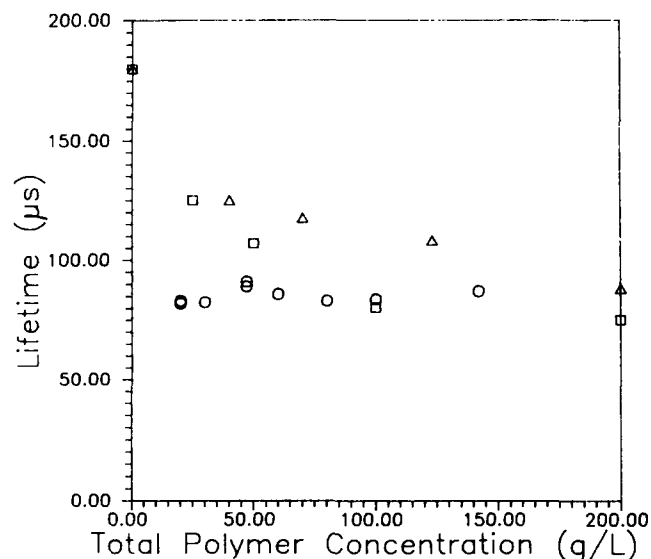

Figure 9 Benzil phosphorescence lifetime as a function of polystyrene concentration in cyclohexane: ($\triangle$) benzil ($1 \times 10^{-3} \, M$) and 47500 polystyrene[30]; ($\square$) benzil ($1 \times 10^{-3} \, M$) and 4000 polystyrene[30]; ($\bigcirc$) 13000 benzil ($1.54 \times 10^{-4} \, M$) end-labelled polystyrene

Table 2 Phosphorescence lifetimes of various molecular weight benzil end-labelled polystyrenes in cyclohexane at 25°C

PS-X-B[a] M_v	Percentage of PS-X-B that is benzil-labelled (%)	PS-X-B conc. (gl^{-1})	Benzil label conc. (gl^{-1})	$\tau \, (\mu s)$
7000	0.8	8.8	1.00×10^{-5}	86
13900	13	20	1.00×10^{-4}	86
170000	13	13	1.54×10^{-5}	91

[a] PS-X-B denotes polymer made with a benzil termination step following end-capping of the living polymer with 1,1-diphenylethylene. Only a fraction of the chains were successfully terminated with a benzil moiety incorporated at the chain end

labelling efficiencies ranging from about 1 to 13%, it should be noted that a higher level of labelling (55%) has recently been achieved on a benzil-terminated polystyrene system with $M_v = 76\,000$. This indicates that the new synthetic technique can be robust with regard to labelling efficiency comparable to the approach used by Horie and Mita[9], who reportedly achieved up to 80% labelling efficiency. (This 80% labelling efficiency was determined by Horie and Mita[9] using u.v.–visible absorbance spectroscopy, which we have found to be relatively insensitive to benzil content in comparison to our phosphorescence intensity calibration technique.)

Photophysical behaviour of benzil in the presence of triplet quencher

When benzil is placed in the presence of a triplet quencher such as anthracene, the lifetime of the benzil molecule is reduced according to the Stern–Volmer equation (equation (2)). It has been found that, when the benzil concentration $\leqslant 1 \times 10^{-4}$ M, an apparent double-exponential phosphorescence decay results. An example of this is shown in *Figure 10*. The effect is the same for both small-molecule benzil and benzil-labelled polystyrenes. It should be noted that, in a previous phosphorescence quenching study of diffusion-limited interactions of benzil and anthracene in polystyrene solutions, Yu and Torkelson[31] maintained the benzil concentration at 1×10^{-3} M and consequently observed only single-exponential decays of benzil phosphorescence.

A proposed photophysical mechanism for this behaviour is given in *Figure 11*. From this mechanism one can see that the apparent double-exponential phosphorescence decay results from absorption of light by benzil at two different times during the phosphorescence decay measurement. The first absorption of light by benzil occurs from the phosphorimeter xenon lamp pulse. The excited-state benzil may dissipate its excess energy through phosphorescence, thermal deactivation or triplet–triplet energy transfer to anthracene (quenching). When anthracene quenches benzil phosphorescence, the excited-state anthracene may dissipate its excess energy by either
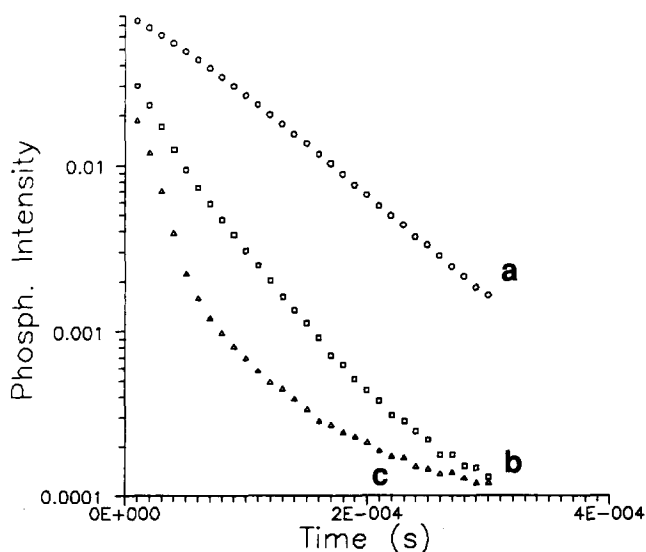
Figure 10 Room-temperature benzil phosphorescence decay in cyclohexane with 1×10^{-6} M anthracene quencher at various concentrations of benzil: a, 1×10^{-3} M benzil; b, 1×10^{-4} M benzil; c, 1×10^{-5} M benzil

$$B + h\nu \longrightarrow B^*$$

$$B^* + A \longrightarrow B + A^*$$

$$\swarrow \quad \searrow$$

$$B + h\nu' \quad B + \Delta$$

$$A^* + A^* \longrightarrow A + A + h\nu''$$
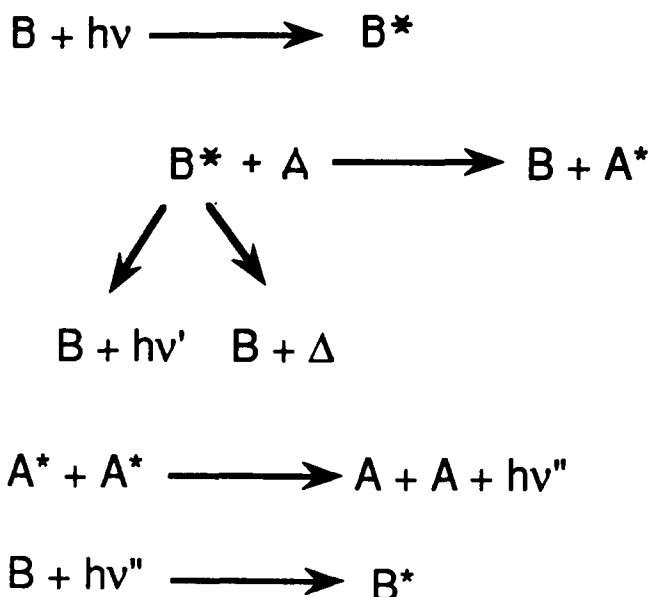
$$B + h\nu'' \longrightarrow B^*$$

Figure 11 Proposed photophysical mechanism to describe double-exponential lifetime decay of benzil in the presence of anthracene quencher: B = benzil; A = anthracene

thermal deactivation or delayed fluorescence. A second absorption of light by benzil may occur from the delayed fluorescence emission from anthracene. An apparent second lifetime results from the second benzil phosphorescence emission. (The photophysical scheme outlined in *Figure 11* may, on a theoretical basis, yield a more complicated phosphorescence decay than double-exponential. However, as the phosphorescence lifetimes associated with any part of the scheme in *Figure 11* except primary absorption and phosphorescence are very long in comparison with the primary absorbance and phosphorescence, these longer lifetimes can be lumped effectively together into a single long lifetime.)

The phosphorescence intensity decay curve can therefore be modelled by the following equation:

$$I(t) = A \exp(-t/\tau_A) + B \exp(-t/\tau_B) \qquad (3)$$

where $I(t)$ is the phosphorescence intensity at time t, A and B are pre-exponential factors (emission intensities at $t = 0$), τ_B is the lifetime of benzil and τ_A is the apparent second lifetime. Since τ_A is very large compared with τ_B and B is much larger than A, it is possible to decouple the lifetime of benzil by examining phosphorescence intensity data only at short times. An example of this decoupling procedure is given in *Figure 12*. When the benzil concentration is sufficiently large ($> 1 \times 10^{-4}$ M), this double-exponential behaviour becomes negligible because only a small percentage of the benzil is now reabsorbing the light emitted by the anthracene quencher, which is kept between 1×10^{-5} and 1×10^{-6} M. This 'reabsorption effect' appears to be a general phenomenon, which occurs with many triplet quenchers of benzil since these same effects are observed when azulene is used as a quencher for benzil.

It should be noted that this non-single-exponential phosphorescence decay has also been observed by Horie and Mita[11]. They attributed this behaviour to anthracene delayed fluorescence and claimed that the decays could be corrected by subtracting out the emission from a 'blank' cell containing only anthracene. However, no fluorescence or delayed fluorescence of anthracene occurs
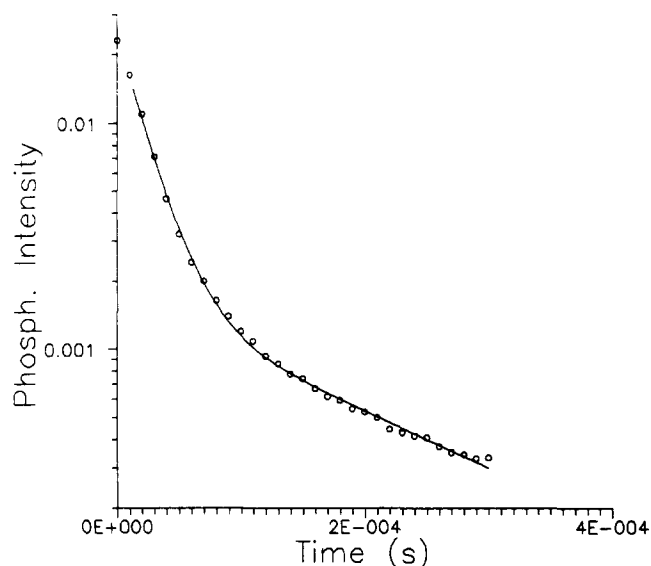
Figure 12 Example of decoupling double-exponential lifetime decay into two lifetimes; 1×10^{-5} M benzil and 1×10^{-6} M anthracene in cyclohexane at 25°C. Solid curve is best fit of double-exponential from Simplex Optimization Program

at the chosen emission wavelength of benzil (560 nm). Indeed, when this experiment was performed by our group, it was confirmed that no emission at 560 nm resulted from solutions containing only anthracene and no significant delayed fluorescence at 560 nm resulted from solutions containing only anthracene-labelled polystyrene.

In order to test the validity of the lifetime decoupling procedure described earlier, the bimolecular phosphorescence procedure described earlier, the bimolecular phosphorescence quenching rate constant, k_q, was determined for small-molecule benzil in toluene at both a high concentration of benzil (1.0×10^{-3} M), where decoupling was not necessary, and a low concentration of benzil (1.0×10^{-5} M), where decoupling had to be performed. For the high benzil concentration system,

$$k_q = (6.22 \pm 0.20) \times 10^9 \, \mathrm{l\,mol^{-1}\,s^{-1}}$$

For the low benzil concentration system,

$$k_q = (6.15 \pm 0.21) \times 10^9 \, \mathrm{l\,mol^{-1}\,s^{-1}}$$

by using the lifetime decoupling procedure previously described. The difference between these two numbers is well within the experimental error for this system. Thus, it can be seen that, over this concentration range, k_q is independent of the benzil chromophore concentration and that the decoupling procedure works well. This fact is very important when studying diffusion-limited interactions with benzil-labelled polymer systems, since the concentration of benzil label will necessarily be reduced as the polymer molecular weight increases or the benzil labelling efficiency decreases.

Bimolecular quenching rate constants

Quenching rate constants have been determined for benzil end-labelled polystyrene being quenched by small-molecule anthracene, small-molecule azulene and anthracene end-labelled polystyrene in cyclohexane. The results are summarized in *Table 3*. As can be seen from the Smoluchowski equation, k_q is proportional to the sum of the self-diffusion coefficients of the interacting

species:

$$k_q = 4\pi R_e \rho (D_A + D_B) \tag{4}$$

where R_e is the characteristic interaction radius between the interacting species A and B, ρ is the collisional efficiency, and D_A and D_B are the diffusion coefficients of A and B, respectively. If the small-molecule diffusion coefficients of benzil, anthracene and azulene were all assumed to be equal, one would expect that the ratio of the polymer–small molecule quenching rate constant to the small molecule–small molecule quenching rate constant (k_{p-s}/k_{s-s}) would have a value of nearly 1/2, assuming that the diffusion coefficient of the labelled polymer is very small compared with that of the small molecule. We see from *Table 4* that the experimental data are not too far from this value, indicating that, although differences in the small-molecule diffusion coefficients do indeed exist, they are not vastly different from each other.

It can be seen from *Tables 3* and *4* that the polymer–polymer k_q for a polystyrene system of $M_v = 13\,900$ is almost an order of magnitude lower than the small molecule–small molecule k_q; this is due to the reduction in the diffusion coefficient of the labels when they are covalently attached to the polymer chain end. From the polymer–polymer data, one can calculate an effective polymer chain-end diffusion coefficient with the Smoluchowski expression:

$$k_{p-p} = 8\pi R_e \rho D_p \tag{5}$$

where R_e is the interaction radius between the chromophore and quencher (benzil and anthracene) labelled on polymer chain ends and D_p is the diffusion coefficient of the labelled polymer chain end. When R_e is taken to be 1.37 nm and ρ is taken to be 0.5 (Ref. 33), D_p is found to be $4.4 \times 10^{-7} \, \mathrm{cm^2\,s^{-1}}$ for the 200 g l^{-1} system of 13 900 PS-X-B being quenched by 13 900 PS-A in cyclohexane.

This value of D_p is only approximate since the value of R_e used here is actually for a benzophenone–naphthalene system. Although the value of R_e is for a

Table 3 Bimolecular quenching rate-constant data (solvent, cyclohexane; temperature, 25°C)

Phosphorophore	Quencher	Polystyrene conc. (g l^{-1})	$k_q{}^a$
Benzil	Anthracene	20	6.00 ± 0.20
13 900 PS-X-B^b	Anthracene	20	4.10 ± 0.71
13 900 PS-X-B	13 900 PS-A^c	20	0.91 ± 0.12
13 900 PS-X-B	13 900 PS-A	200	0.45 ± 0.07
13 900 PS-X-B	Azulene	20	2.88 ± 1.41

^{a} Units are $1 \times 10^9 \, \mathrm{l\,mol^{-1}\,s^{-1}}$
^{b} PS-X-B is benzil-terminated polystyrene that was end-capped with 1,1-diphenylethylene prior to termination
^{c} PS-A is anthracene end-labelled polystyrene

Table 4 Ratios of bimolecular quenching rate constants for various systems in cyclohexane at 25°C^a

System	k_{p-s}/k_{s-s}	k_{p-p}/k_{s-s}	k_{p-p}/k_{p-s}
Benzil–Anthracene	0.68	0.15	0.21
Benzil–Azulene	0.48	–	–

^{a} Polystyrene concentration is 20 g l^{-1} for all of the above data. $M_v = 13\,900$ for all labelled polymer. The subscript 'p' denotes labelled polymer and the subscript 's' denotes the small molecule

different system, it is the best value to use at this point in time, as no R_e data are available on the benzil–anthracene system. These values of k_{p-p} and D_p are in general agreement with data obtained by Horie and Mita[11], who also used this value of R_e in evaluating D_p from k_q data for their benzil-labelled polystyrene system.

In the future, the relationship between diffusion-limited interactions of polymer chain ends and polymer self-diffusion coefficients D_s will be explored by comparing the concentration and molecular-weight dependence of k_q (or equivalently D_p from equation (5)) with those of D_s. This will help determine whether the polymer self-diffusion coefficient or other diffusional processes dominate polymer–polymer diffusion-limited interactions. At present, it is interesting to note that $D_p\eta$ (where η is solvent viscosity) for our 200 g l^{-1} $M_v = 13\,900$ polystyrene system in cyclohexane is approximately two times greater than $D_s\eta$ for the 223 g l^{-1} $MW = 32\,000$ polystyrene system in THF studied by Wesson et al.[5] and about four times greater than $D_s\eta$ for the 380 g l^{-1} $MW = 10\,000$ polystyrene system in THF studied by von Meerwall et al.[33]. Better comparisons can be afforded in the future by running phosphorescence quenching and forced Rayleigh scattering experiments on identical systems.

The technique of phosphorescence quenching provides a valuable tool with which to probe the dynamics of site-specific diffusion-limited interactions occurring in polymer systems. Using benzil-labelled polymers as a model, we plan to investigate the effects of polymer concentration and molecular weight, and thereby the possible effects of interpolymer entanglements, on the termination reaction in free-radical polymerization and related processes. Preliminary information for the polymer–polymer k_q at higher polymer concentrations has already been obtained. *Table 3* shows a comparison for the polymer–polymer k_q for $M_v = 13\,900$ polystyrene in cyclohexane at 20 and 200 g l^{-1}. At 200 g l^{-1}, k_q is about one-half of the k_q at 20 g l^{-1}. This reduction in k_q is due to a reduction in the diffusion coefficient of the polymer molecule and of the chain end.

Work under way includes a detailed study of how polymer solution parameters relate to the onset and the severity of the 'gel' effect in free-radical polymerization. In addition, by producing benzil-terminated poly(methyl methacrylate) as well as benzil-terminated polystyrene, a quantitative understanding of the causes of the difference in the 'gel' effect exhibited by poly(methyl methacrylate) and polystyrene systems may be obtained.

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