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Photon Correlation Spectroscopy of Poly(vinyl acetate)

In recent reports, Wang and Fischer[1] have presented a theoretical derivation which leads to the conclusion that the photon correlation function of light isotropically scattered by bulk amorphous polymers near the glass transition temperature is equivalent to a measurement of the time-dependent longitudinal compliance. This conclusion was bolstered by an experimental study[2] of light scattered by poly(vinyl acetate) (PVac) in which the relaxation spectrum evaluated from the photon correlation data was found to be closely similar to that which characterized the bulk compliance of PVAc by McKinney and Belcher.[3]

In the discussion of their PVAc light scattering data, Fytas et al. note[2] that their data are not in agreement with an earlier study in our laboratory.[4] They assign the discrepancy to the analytical problems which derive from the splicing procedures used to generate correlation functions in our study. By contrast, their experiment utilized a logarithmic correlator, thus avoiding the need to splice data sets. While this experimental difference may influence the comparison of their data with ours, we write this paper to point out that the difference between the two studies is, in fact, for the most part due to the difference in glass transition temperatures of the two samples. The sample used in our study[4] was of molecular weight $M_w = 4.4 \times 10^6$ and $T_g = 32 \pm 2$ °C; for the sample of Fytas et al.[2], $M_w = 15\,000$ and $T_g = 17$ °C. It is not therefore surprising that at comparable temperatures, the average relaxation times $\langle\tau\rangle$ measured by Fytas et al.[2] are several orders of magnitude larger than ours.

To illustrate this, we have plotted in Figure 1 relaxation time data in the form log $\langle\tau\rangle$ vs. $(T - T_g)$, the temperature distance from T_g. Clearly, our $\langle\tau\rangle$ values are reasonably consistent with those of Fytas et al.[2] for $(T - T_g) \sim 15$ °C. However, Figure 1 indicates that, for our data which extend into a temperature regime closer to T_g, the apparent activation energy is significantly smaller than would be calculated from the WLF equation which fits the data of Fytas et al.[2] A further difference between the two sets of data is that, as stated by Fytas et al.[2], the exponent β, estimated from fractional exponential fits to experimental correlation functions, i.e., $\phi = \exp(-t/\tau)^\beta$, is found to be somewhat larger in our work (0.45 vs. 0.35).

These differences may indeed be the result of the errors attendant to analysis of spliced correlation functions as

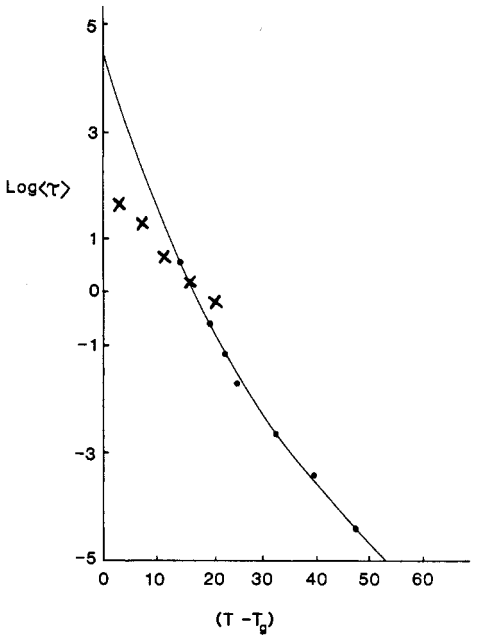

Figure 1. Logarithm of the average relaxation time derived from photon correlation analysis of light isotropically scattered by poly(vinyl acetate) in the bulk state near T_g, plotted vs. the temperature distance $(T - T_g)$: (●) data of Fytas et al.;[2] (×) data of Tribone et al.;[4] the solid line is a WLF fit to the data of Fytas et al.

stated by Fytas et al.[2] However, it is worth noting that at least two studies[5,6] have observed that the apparent activation energy of viscoelastic properties just above or below T_g may be smaller than that predicted by extrapolation based on the WLF equation applicable for $T \gg T_g$. Also, for a low-T_g polymer, it is possible that the width of the relaxation spectrum may be increased because of the molecular weight distribution and the associated spread in T_g. This could be a contributing factor in the smaller β-parameter observed by Fytas et al.[2] Definitive comparison between different experimental data sets under circumstances where T_g is molecular weight dependent requires identical or at least closely similar samples.

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Registry No. PVAc, 9003-20-7.

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Solid-Phase Block Copolymer Synthesis by the Iniferter Technique

In 1982 we proposed the concept of an iniferter (*ini*tiator–trans*fer* agent–*ter*minator) for design of polymer

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Table I
Block Copolymerization of MMA with 2 as PSG Photoiniferter[a]

time, h	tot polymer, g	conv of MMA,[b] %	extraction: graft polymer, g	extraction: homo(PMMA),[c] g	conv of MMA grafted, %	block copolymer[d]: yield, g	block copolymer[d]: $\bar{M} \times 10^{-4}$ (GPC)[e]
0	(0.80)	(0)	(0)	(0)	(0)	(0.42)[f]	(1.9)[f]
2.5	2.35	20.6	2.22	0.13	18.9	1.84	6.9
5.0	2.98	29.0	2.74	0.24	25.8	2.36	7.6
7.5	3.41	34.7	3.06	0.35	30.1	2.68	8.0
10.0	3.64	37.8	3.20	0.44	31.9	2.82	9.2

[a] **2** (content of PSt grafted = 53.0%), 0.80 g; MMA, 8 mL; benzene, 4 mL; 30 °C. [b] Calculated from the weights of MMA polymerized and used initially. [c] Isolated by extraction with benzene. [d] Isolated by hydrolysis of PSG-*g*-(PSt-*b*-PMMA). [e] Without calibration. [f] Indicated values for poly(St) isolated by hydrolysis of PSG-*g*-PSt used.

chain-end structure.[1] Simultaneously, we used some iniferters to propose a new model for living radical polymerization in a homogeneous system.[2] Among the iniferters used, *N*,*N*-diethyldithiocarbamate (DC) derivatives were found to be excellent photoiniferters for the syntheses of various functional, block, graft, and cross-linked polymers.[1-9]

Previously, we synthesized some multicomponent block copolymers using tetraethylthiuram disulfide (TD) as a starting photoiniferter.[4] E.g., triblock copolymer was obtained as follows: the polymerization of a second monomer with the polymer produced by TD as a polymeric photoiniferter gave a block copolymer, which was then used as a photoiniferter for the polymerization of a third monomer, yielding a triblock copolymer. However, pure triblock copolymer free from homopolymer could not be isolated by solvent extraction, because no suitable solvent for separation was found.

In 1963 Merrifield[10] reported a brilliant solid-phase peptide synthesis using a reagent attached to the polymer support. If a similar idea can be applied to the iniferter technique, pure block copolymers could be synthesized by radical polymerization.

Thus, if DC attached to a polystyrene–gel (PSG) through a hydrolyzable ester spacer is used as a photoiniferter, pure multiblock copolymers free from homopolymer may be obtained by a repeated cycle of photopolymerization and solvent extraction of the homopolymer produced, followed by hydrolysis, as shown in Scheme I.

The present paper describes the synthesis of pure block copolymers using PSG modified by DC (**1**) as a photoiniferter. Benzyl (*N*,*N*-diethyldithiocarbamyl)acetate (BDA) was used as a model photoiniferter.

PSG (Kodak PSt–2% divinylbenzene copolymer beads, 200–400 mesh, ca. 34% swollen in benzene) was extracted with THF and chloromethylated with chloromethyl ethyl ether in carbon tetrachloride; 33 mol % St unit in PSG was chloromethylated. This was then reacted with potassium (*N*,*N*-diethyldithiocarbamyl)acetate in DMF to yield **1**, which contained 22 mol % DC (model methyl *N*,*N*-diethyldithiocarbamate: λ_{max}(N—C=S) 278 nm, ϵ 12 500 in acetonitrile). Photopolymerizations were carried out at 30 °C under UV light (Toshiba SHL-100 UV-2). After polymerization for a given time, the polymerizing mixture was poured into excess methanol to precipitate the polymer, which was then extracted with benzene in a Soxhlet extractor for 24 h to separate polymer grafted onto **1** and homopolymer. The number-average molecular weight ($\bar{M}_n$) of polystyrene was determined by GPC calibrated with standard polystyrenes.

Photopolymerization of styrene (St) with BDA was observed to proceed in a manner similar to the living radical mechanism proposed previously;[2,3] i.e., both yield and $\bar{M}_n$ of the polymers increased with reaction time, as shown in Figure 1. Similarly, **1** also served as an excellent PSG photoiniferter, and the grafting of St (M_1) onto PSG (**2**) proceeded in greater than 90% yield after complete extraction of the homopoly(St) with benzene. Then **2** was hydrolyzed with sodium hydroxied in water/tetrahydrofuran or sodium methoxide in methanol, and the poly(St)

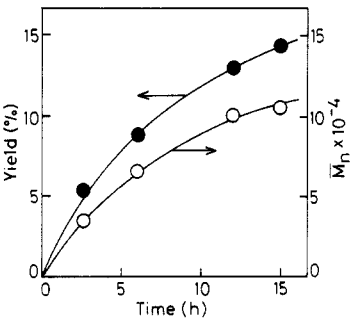


Figure 1. Time–yield and time–$\bar{M}_n$ relations for bulk polymerization of St with BDA as a photoiniferter at 30 °C. [BDA] = 2.4×10^{-2} mol/L.

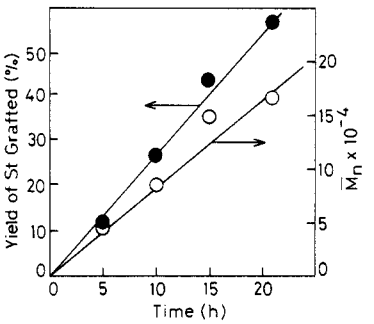
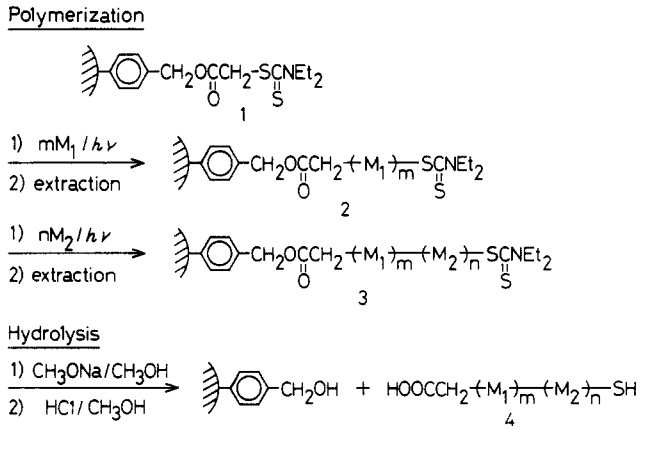


Figure 2. Time–yield and time–$\bar{M}_n$ relations for poly(St) isolated by hydrolysis of the graft polymer of St onto PSG, PSG-*g*-PSt, obtained. Polymerization conditions: **1**, 0.80 g; St, 8 mL; benzene, 4 mL; 30 °C.

Scheme I



separated from **2** was isolated. The yield and M_n of these poly(St)'s were found to increase with reaction time, as shown in Figure 2, indicating that these graft copolymerizations also proceeded via a living radical mechanism similar to the case of BDA.

Moreover, the graft polymer **2** was observed to act as a photoiniferter of radical polymerization of methyl methacrylate (MMA, M_2), as shown in Table I. After extraction of homopoly(MMA) and hydrolysis of the resulting graft–block copolymer attached to PSG (**3**), a block copolymer of poly(St) with poly(MMA) (**4**) was isolated by extraction of benzene. Yield and molecular weight increased with reaction time.

From GPC measurement, however, the block copolymer **4** thus obtained was observed to contain ca. 10% homopoly(St), even after a prolonged reaction time (20 h). These results were in agreement with those observed for the block copolymer synthesis using DC photoiniferters.[4,6] The formation of the homopoly(St) might be due to part of the DC iniferter groups at the grafted poly(St) chain end in **2** being destroyed during polymerization, as a result of the previously reported[2] deviations from ideal living radical polymerization.

To avoid homopoly(St) formation, TD (0.03 mol/L), which can dissociate into *N,N*-diethyldithiocarbamate radicals,[1] was added to the photopolymerization system of St with **1** (see Figure 2 for conditions). When **2** thus obtained was used as a PSG photoiniferter for the polymerization of MMA, followed by extraction and hydrolysis of the resulting graft–block copolymers (**3**), a block copolymer of poly(St) with poly(MMA) which contained only a trace of homopoly(St) was isolated. The block copolymer **4** thus obtained was confirmed by GPC to be pure and free from homopolymer.

The graft–block copolymer consisting of St–MMA blocks attached to PSG (**3**), obtained by the polymerization of MMA in the presence of **2** and TD, was confirmed to induce further photopolymerization, leading to pure PSt-*b*-PMMA-*b*-PSt triblock copolymers. Moreover, tricomponent triblock copolymer, PSt-*b*-poly(*p*-chlorostyrene)-*b*-PMMA and PSt-*b*-PMMA-*b*-poly(methyl acrylate), were synthesized by a similar technique.

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Registry No. PSt, 9003-53-6; BDA, 3052-61-7; (St)·(MMA) (copolymer), 25034-86-0; KDC, 686-07-7.

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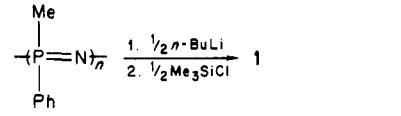
Silylated Derivatives of Poly[methylphenylphosphazene][1]

The preparation of polyphosphazenes with alkyl and aryl substituents directly attached to phosphorus by carbon–phosphorus bonds has been accomplished by thermolysis of *N*-silylphosphoranimines, $Me_3SiN{=}P(OCH_2CF_3)RR'$, where R, R′ = Me, Et, Ph[3]. With the availability of these simple polymers, we have now begun to investigate synthetic approaches to other polyphosphazenes with more diverse substituents attached to the backbone via P–C bonds. These new systems could possess such useful properties as higher thermal stability, unusual solubility characteristics, and enhanced mechanical and surface properties and might also contain reactive sites for cross-linking, binding of transition metal catalysts, or interaction with biological systems.

We are investigating three methods of altering the substitutents at phosphorus. These are (1) synthesis of new primary phosphine precursors, $(Me_3Si)_2NPRR'$, where R and R′ are more complex alkyl and aryl moieties, (2) alteration of R and R′ in the immediate *N*-silylphosphoranimine precursors, $Me_3SiN{=}P(OCH_2CF_3)RR'$, and (3) alteration of R and R′ in preformed poly(alkyl/arylphosphazenes) such as $[Ph(Me)P{=}N]_n$. We report here our first results related to the latter approach. In these cases, a methyl group attached to the P–N backbone is the site of derivatization.

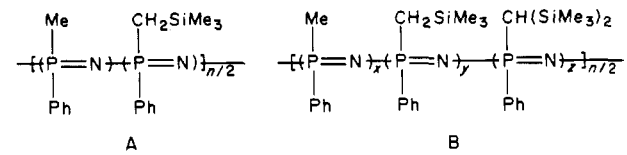
Methyl groups attached to phosphorus in both cyclic phosphazenes[4] and in *P*-methyl-*N*-silylphosphoranimines[5,6] have been deprotonated with alkyllithium reagents. In this study we found that a portion of the methyl groups in poly[methylphenylphosphazene][3b] can be deprotonated by *n*-BuLi. When a 0.6–1.0 M solution of $[Ph(Me)PN]_n$ in THF at −78 °C was treated with 0.5 equiv of *n*-BuLi, stirred for 1.5 h, and quenched with 0.5 equiv of Me_3SiCl (eq 1), a new polymer[7] **1** was obtained. Elemental analysis



(1)

(Table I) of **1** indicated that complete reaction had taken place, i.e., that 0.5 equiv of Me_3Si groups were incorporated into the polymer. More importantly, GPC analysis of **1** showed that no cleavage of the P–N backbone occurred. Due to the incorporation of the Me_3Si group, the $\bar{M}_w$ of **1** (73 000) was, as expected, 26% higher than $\bar{M}_w$ of the parent polymer, $[Ph(Me)PN]_n$ (58 000) (Table II). Furthermore, the molecular weight distributions (Figure 1) of the parent and derivative were virtually identical. Intrinsic viscosity measurements (Table II) also verified the lack of chain degradation. Although cleavage of the P–N backbone occurs when poly(halophosphazenes) are treated with organolithium reagents,[8] the milder conditions of this reaction presumably prevented a similar problem.

The simplest representation of **1** is formula A, the logical product if the reaction proceeds by initial CH_2^- anion formation followed by quenching with Me_3SiCl. The ^{31}P



A B

NMR spectrum of **1**, which consisted of two broad singlets (δ ($CDCl_3$) 4.8, 0.5) of approximately equal intensity, supports formula A. The ^1H and ^{13}C NMR spectra,[9] however, suggested that deprotonation and substitution

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