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Photoreaction of poly(ferrocenylmethylsilane-co-phenylmethylsilane) in solution

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Abstract

The photoreaction of $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ in solution, Fc = ferrocenyl = $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$, is reported using a coupled gel permeation chromatography/light scattering system. The presence of the ferrocenyl substituent resulted in a significant retardation of the depolymerization process and the process has been monitored in terms of changes in the percent of initial mass, molecular weight, polydispersity and molecular conformation. The results indicate that photo-scission of silicon–silicon bonds occurred preferentially at the polymer chain termini. The results have been compared to those obtained from the photodegradation of poly(phenylmethylsilane) previously reported of approximately the same molecular weight.

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1. Introduction

The study of organometallic and inorganic polymers has become an area of considerable interest since such systems can be useful precursors to novel materials unavailable from other sources [1]. The addition of transition metals substituent to silicon-containing polymers can be expected to modify several properties of the material including thermal stability, redox, magnetic and optical behavior. The development of ferrocenylsilanes illustrates the potential of this type of materials where the organometallic cores may function as semiconductors, variable refractive index-sensing materials, or precursors to magnetic nanostructures, etc. [2,3]. On the other hand, upon irradiation with ultraviolet light, polysilanes exhibit a characteristic chain scission depolymerization, a source of their potential as photo-resistant materials. We have reported that polysilanes

containing the ferrocenyl pendant substituent, $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$, (Fc, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$) exhibited a photochemical stabilization with respect to depolymerization [4,5]. In the same report, doping experiments were performed using varying amounts of FcH added to $(\text{PhMeSi})_n$. The varying amounts of FcH corresponded to the quantity of Fc incorporated in the homopolymer. The results indicate no significant reduction in photodepolymerization of the polysilane. Furthermore, electrochemical analysis of these polymers indicate a small interaction of the redox active Fc groups with the polysilane chain [6].

We have also reported that the coupled system gel permeation chromatography/light scattering (GPC/LS) is a powerful tool for studying the photodegradation of polysilanes and copolysilanes [7,8]. Now, this technique is being applied to investigate in detail the nature of the apparent stabilization of the polysilane chains by the Fc substituent. Specifically we report the photoreaction in terms of changing mass, molecular weight distributions, polydispersity and the molecular conformation behavior during the irradiation process.

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2. Experimental

The synthesis and purification of $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ was described in detail previously [4]. The copolymer sample ($M_w = 725\,000$ Da) was dissolved in degassed tetrahydrofuran (HPLC grade Fisher Chemical) and the resulting solutions were purified by filtration through a membrane of $0.22\ \mu\text{m}$ pore size. The copolymer was irradiated with a Hitachi GL-15 Hg lamp. The spectral lines were 254.5, 313.5, 365, 405, 408, 436, 546, and 576.5 nm. The corresponding energies were 112.4, 91.2, 78.4, 70.6, 70.1, 65.6, 52.4, and 49.6 kcal mol⁻¹. The Exposure times were 5, 8, 10, 15, 20, 30 and 40 s. The irradiation process was evaluated by the GPC/LS system.

The GPC measurements were performed in a GPC system equipped with a model Varian-9012Q pump, a Waters-2410 Refractive Index Detector, and a US-5298 manual injector with a THF mobile phase constant flow rate of $1\ \text{ml min}^{-1}$. Two columns were used: a PLGel with nominal porosities of $100\ \text{\AA}$ and a Lineal Waters Styragel HR5E. The Dawn Model F LS detector from Wyatt Technology Corporation was coupled on-line with the GPC. UV spectra were determined in THF solutions in a Perkin–Elmer Lambda 5 UV–vis Spectrophotometer. The concentration of the solution was $1.00 \times 10^{-4}\ \text{g ml}^{-1}$.

The differential refractive index increment (dn/dc) at 632.8 nm for $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ was calculated with the mass conservation using the GPC/LS system. The photolysis of the copolymer was analysed using the same system. It is possible to measure the scattered intensity at 15 angles as the samples elute. The eluant from the GPC was directed to the LS detector. The molecular weight can be evaluated across the whole chromatogram if a concentration-sensitive detector, usually a refractive index detector (IR), is connected in line with the multi-angle laser light-scattering photometer. This technique eliminates the need for a column calibration. Mass measurements by means of this system have been described in detail [8]. The value was used to monitor the M_w copolymer changes upon exposure to an UV source. All GPC/LS experiments were carried out at room temperature.

¹H-, ¹³C- (at 300 and 75 MHz, respectively) and ²⁹Si-NMR spectra were obtained in C₆D₆ solutions using a Varian Unity-Plus 300 MHz NMR Spectrometer. ²⁹Si- and ¹³C-NMR spectra were determined also in solid state by CPDAS sequence in the same spectrometer (²⁹Si resonance at 60 MHz).

The copolymer sample was characterized using the GPC/LS and NMR: ¹H-NMR (C₆D₆) δ 6.8 (br d m, C₆H₅), 3.8 (br d m, C₅H_n), -0.26 , -0.45 (br d s Si-CH₃); ¹³C-NMR (C₆D₆) δ 137, 135, 126 (br d s, C₆H₅), 73, 68 (br d s, C₅H_n), -6.1 (br d s, SiCH₃); ²⁹Si-NMR (C₆D₆) δ -39 , -39.6 , -41 and solid state NMR;

¹³CCPMAS, δ 135, 127 (C₆H₅), 72 (C₅H_n), -5.1 (SiCH₃); ²⁹SiCPMAS, δ -29.1 . Differential scanning calorimetry was carried out with a DSC from Mettler Toledo Star System. The scan rate was $10\ ^\circ\text{C min}^{-1}$ and the sample was kept under a nitrogen atmosphere. The sample was cooled down to $-10\ ^\circ\text{C}$ at a rate of $10\ ^\circ\text{C min}^{-1}$ then heated at $150\ ^\circ\text{C}$ as the DSC curve was recorded. The DSC curve exhibited a second-order transition at $55.73\ ^\circ\text{C}$, which corresponds to the copolymer Tg.

3. Results and discussion

As expected, the ²⁹Si-NMR spectra of the starting copolymer showed a pattern that suggests partial tacticity as reported previously for aryl polysilanes [9].

The dn/dc value was $0.184\ \text{ml g}^{-1}$. The copolymer M_w in THF was determined also by GPC/LS system measurements and the value was $725\,000$ Da, with a polydispersity of $(M_w/M_n) = 1.19$. The SEC chromatogram showed a monomodal curve from the simultaneous observation of IR and LS detectors and the square root of the mean square radius (RMS) = $52.8\ \text{nm}$. The copolymer exhibits a UV absorption maximum at $342\ \text{nm}$, similar to that observed for the homopolymer (PhMeSi)_n. The ratio PhMeSi to FcMeSi reported was 20:1 [4].

The molecular weight of the Fc-containing copolymer of $725\,000$ Da is in total agreement with the high molecular weight reported by Pannell et al. for these materials [5]. The discussion is closely related to the (PhMeSi)_n homopolymer studied previously in the same system [7] under the same irradiation conditions. This homopolymer has a molecular weight of $606\,000$ Da. The photobleaching process of the Fc-containing copolymer is illustrated in Fig. 1. Relevant information is illustrated at the irradiation times of 0, 5, 10, 15, 20, 25 and 30 s. The initial observation of Pannell et al. was that a certain degree of photostabilization was introduced in the polymer in proportion to the amount of metal incorporated. Although the ratio of PhMeSi to FcMeSi substituents was 20:1 and it has been reported that the degree of photostabilization introduced by the metal substituent is proportional to the amount of metal incorporated (5:1 more photostable than 20:1), the depolymerization process is retarded with respect to (PhMeSi)_n photobleaching process. Fig. 1 shows an apparent important change from 0 to 5 s of UV exposure, then at 10 and 15 s the curves practically overlap. The same happened at 20 and 25 s, and then some decay in the absorption curve at an exposure time of 30 s. During these irradiation periods the absorption maximum shifts from 342 to $340\ \text{nm}$. In polysilanes, as the number of silicon atoms increases the energy of the electronic transition decreases. The absorption wave-

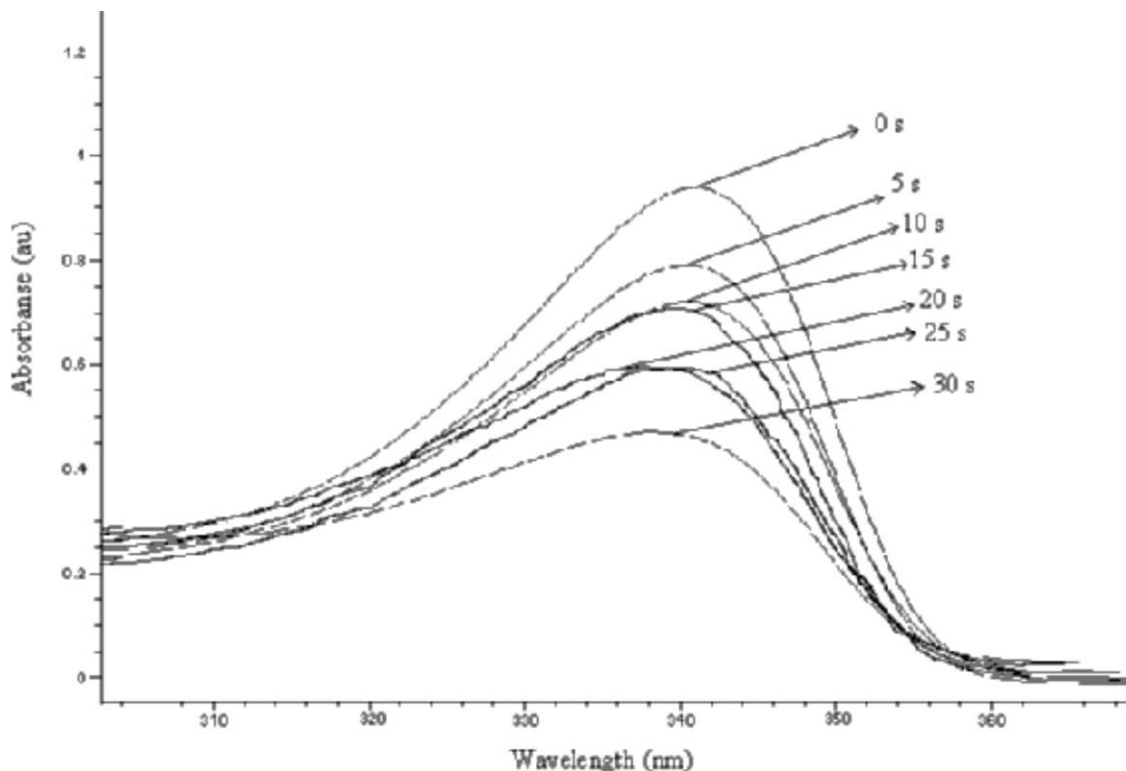


Fig. 1. Photobleaching of THF solutions of $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ with Hg lamp to several absorption times (0, 5, 10, 15, 20, 25, 30 and 40 s).

length therefore increases and eventually reaches a limit when the number of silicon atoms is about 30 [1]. Thus, due to the fact that the copolymer sample used in this work is of high molecular weight (725 000 Da), the small progressive blue shift does not necessarily denote that the irradiation process in some periods is not accompanied by a significant decrease in molecular weight. But, moreover the GPC/LS measurements clearly indicate that this effect is accompanied by a slow decrease in the $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ average molecular weight.

Keeping in mind the possibility to follow in more detail the irradiation process using the coupled GPC/LS system, the discussion is directed to several properties such as mass, molecular weight, conformation and polydispersity behavior in order to obtain a better demonstration of the effect of ferrocenyl ligands on the depolymerization process retardation.

The copolymer mass decreases during UV exposure as evidenced by GPC/LS measurements (Fig. 2). This system gives information on the eluted mass using the dn/dc value to calculate the concentrations at each elution volume and the mass recovery from the columns. In the initial period of exposure (0–5 s), the polymer mass is reduced only from 9.2×10^{-6} to 8.1×10^{-6} g. The latter value corresponds to 91% of the initial mass. The soluble fraction mass between 11.5 and 14 ml of elution volume is 4.85×10^{-5} g, which is equivalent to 60% of the total eluted mass in the first exposure time. In the irradiation of $(\text{PhMeSi})_n$ with the same source

and the same exposure period, the mass was reduced to 63% of the initial mass and the soluble fraction mass is now equivalent to 27% of the total eluted mass [7]. It has been reported that during the photolysis of this homopolymer with UV light ($\lambda = 254$ nm), the major reactions are homolysis, to give various intermediates by elimination such as silyl radicals and silylene [1]. After 8 s of exposure, the copolymer mass was reduced to 67% of the initial mass and the fractions whose hydrodynamic volume showed an increment are reduced to 34% of the total eluted mass. Note that there was much less difference in the polymer mass between 8 and 10 s of

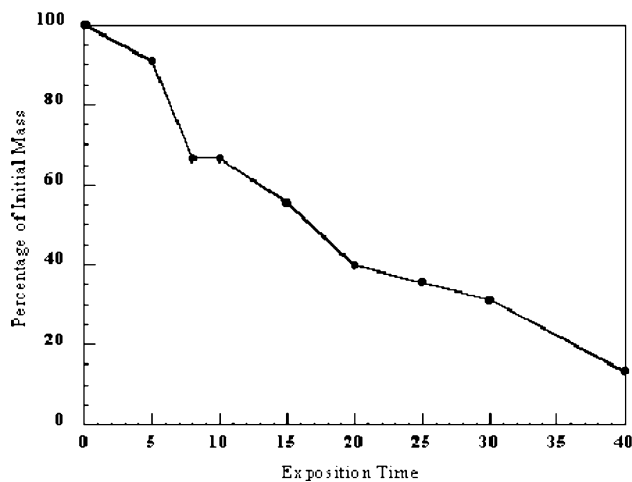


Fig. 2. Change in the percentage initial mass as a function of UV absorption time using a Hg lamp.

exposure time but the fractions (see again Fig. 2), which show an increase in the molecular weight at a low retention time decreased to 26% of the total eluted mass (Fig. 3). This Fig. 3 shows an increase in the molecular weight at a low retention time. In typical chromatograms the very large molecules moved through the column quickly (species with lower retention time) and the smaller molecules were retained (species of higher retention time).

This unusual behavior in the interval from 10.75 to 11.5 ml of elution volume was observed with the coupled system (GPC/LS). This behavior was due to the presence of fractions whose hydrodynamic radius increased, e.g. fractions that show some cross-linking.

The above results suggest that the presence of ferrocenyl substituents in the $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ resulted in a significant retardation in the mass decreases and also a reduction in the copolymer concentration of the species with increase in the hydrodynamic volume. Thus, between 0 and 10 s the copolymer mass is slightly reduced, however, the species with increase in hydrodynamic volume are significant (see first slope at the left part of Fig. 3). These species disappear at 15 s of UV exposure. According to these results, the copolymer mass behavior may indicate that the radiation-induced copolymer mass is reduced by a chain scission process, essentially at the chain termini. Between 15 and 40 s the copolymer mass is continuously reduced and finally, after 40 s the $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ mass was 13.33%. This interval behavior is probably related to a random chain scission process. However, fragments of high molecular weight and low concentration are still observed in the LS detector. If we compare this behavior to the $(\text{PhMeSi})_n$ photolysis process, in this case the initial mass was converted to radicals, cations, anions, excited molecules, and fragments of low molecular weight and

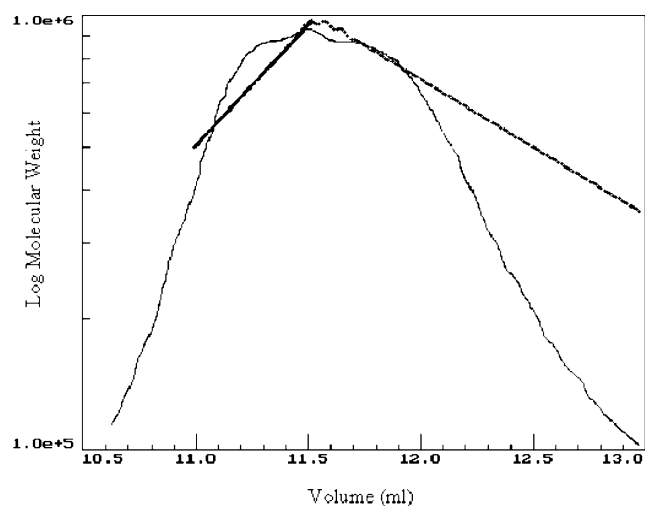


Fig. 3. Molecular weight as a function of elution volume after 5 s of UV exposure using a Hg lamp. Overlay: the signal of the IR detector without scale.

low concentrations. These fragments are actually observed in the RI detector, but are not observed in the LS detector due to the noise level that is higher in this detector.

The UV radiation effect on the copolymer weight-average molecular weight (M_w) is shown in Fig. 4. The M_w as a function of UV exposure times shows small changes at the beginning of the irradiation process. Between 0 and 10 s of exposure two processes were observed: first a diminution of the fractions that show an increase in the molecular weight at low retention time and second a non-substantial degradation of the copolymer. The GPC/LS measurements provide evidence that an exposure time of 15 s is needed to reduce the M_w from its initial value of 7.2×10^5 to 6.0×10^5 Da, a value corresponding to 83.3% of the initial M_w . At the same UV exposure time, the molecular weight reduction as a function of elution volume is given by a typical GPC experiment. $(\text{PhMeSi})_n$ irradiated with the same source [7] showed the following effects: at the beginning of the process the $(\text{PhMeSi})_n$ shows an increase in the molecular weight at low retention time and the M_w was reduced to 20% of the initial M_w . As well, in the case of $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ the double slope disappears at 15 s of UV exposure. Recall that organosilane polymers, with phenyl pendant groups directly attached to the main chain, show a tendency to cross-link by UV radiation [10]. It seems to be clear that the effect of the incorporation of pendant ferrocenyl into polysilane is necessary to explain the molecular weight behavior. In the interval from 15 to 30 s of UV exposure, degradation occurs (M_w/M_n increases) because of a chain scission process; however, this is not accompanied by a significant decrease in molecular weight. After 40 s of UV absorption, the M_w (M_w/M_n decrease) is reduced to 67% of its original value. Again, it is evident that this behavior is quite different from the one observed for $(\text{PhMeSi})_n$. Thus, apparently, the phenyl groups that

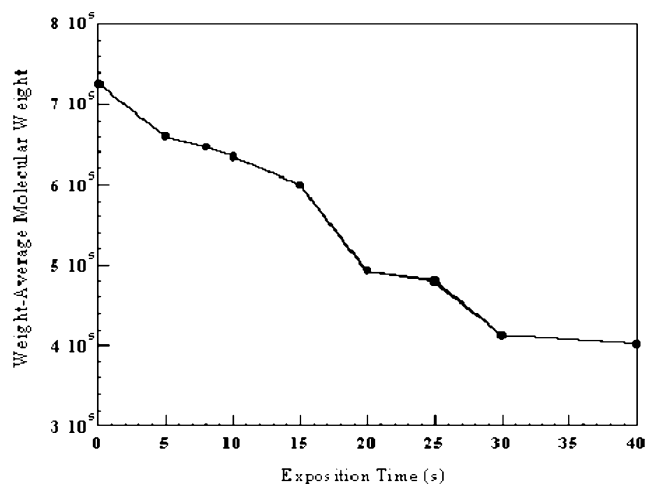


Fig. 4. Change in the weight-average molecular weight as a function of UV absorption time using a Hg lamp.

photochemically induce chain destabilization generating species whose hydrodynamic volume tend to increase compete against Fc substituents that photochemically stabilize the chain resulting in depolymerization retardation during the UV irradiation process.

Practically no change is detected in the $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ polydispersity in the interval 0–15 s (Fig. 5). In this period, the average molecular weight decreased strikingly slow owing to homolytic reactions near the copolymer chains termini (photodepolymerization). This is confirmed by the fact that the polydispersity was almost constant [10]. In this process, the chain-lengths determined as the average number of monomer molecules formed per main chain scission were very small. It is typical of a depolymerization process. It is quite possible that the depolymerization process depends on two features of the chromophoric segment, i.e. length and the presence of more Fc groups in the main chain. A similar polydispersity behavior is observed in the $(\text{PhMeSi})_n$ irradiation but its M_w is strongly degraded [7]. Polydispersity of the copolymer increases between 15 and 30 s of UV exposure from $M_w/M_n = 1.19$ to 2.4. This may indicate that the major reactions are homolysis by a mainly random process. In the interval 30–40 s of UV exposure the $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ polydispersity surprisingly decreases from $M_w/M_n = 2.4$ to 1.3 but no substantial polymer degradation was observed. A tentative interpretation considers that in such period some copolymer chains are more stable after UV irradiation, regrouping chains of similar molecular weight to get a diminution in the copolymer polydispersity. This behavior probably can be correlated to the slight decrease in the copolymer molecular weight. According to the above results, it is likely again that the presence of the Fc substituents in the copolymer induces interesting differences in the $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ photoreaction process in solution.

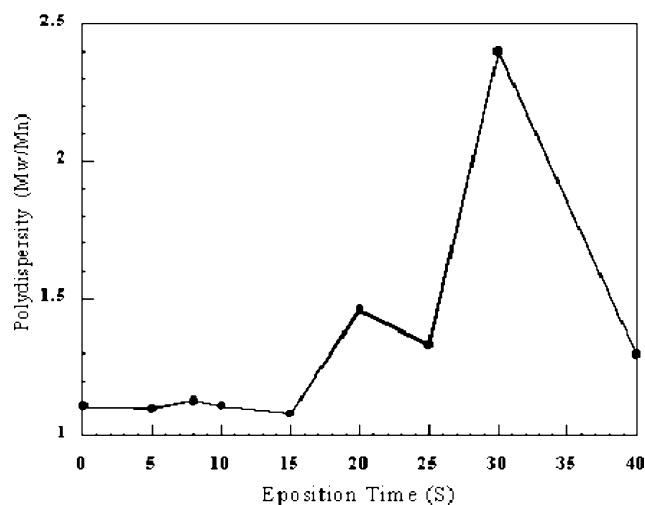


Fig. 5. Change in the polydispersity M_w/M_n as a function of the UV absorption time using a Hg lamp.

The effect on the molecular conformation was also evaluated by the GPC/LS Coupled System. The molecular conformation is determined from the square root slope of the mean square radius plotted against the log of the molecular weight. Thus, the $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ original sample exhibited a slope of 0.6 that is related to random coil (Fig. 6). West reported that polysilanes may form random coils in solution [10]. After 8 s of UV exposure the slope ($P=0.7$) between 10.8 and 11.5 ml of elution volume identifies fractions with a more extended conformation, e.g. with properties intermediate between those of rigid rods and those of highly flexible coils. When the solution is exposed for 10 s to the Hg lamp, fractions whose hydrodynamic radius increased were observed between 11 and 11.4 ml of elution volume, while rigid rod chains ($P=1$) dominate in the remaining region (11.4–14 ml elution volume). After 15 s of UV exposure the conformation is consistent with a rigid rod polymer chain ($P=1.1$). While in the interval from 0 to 15 s with the same source, $(\text{PhMeSi})_n$ shows the following conformation set: (1) semiflexible ($P=0.7$, original polymer), (2) species whose hydrodynamic radius increased and fractions with conformation nearly rigid rod ($P=0.9$), and (3) semiflexible ($P=0.7$) [7].

Theoretical as well as experimental evidence indicate that λ_{\max} increases as the number of *trans*-Si–Si–Si–Si conformation increases [1]. The λ_{\max} of $(\text{PhMeSi})_n$ depends on the length of the non-interrupted Si–Si bonds and decreases with increasing exposure to the Hg lamp, therefore the number of *trans*-Si–Si–Si–Si conformation decreased and hence the rigidity is reduced, but in the $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ after 15 s of UV exposure the weight-average molecular weight is still very high (6×10^5 Da) so, between 15 and 25 s of UV absorption, the copolymer continues showing a rigid rod conformation. According to this behavior, it is quite

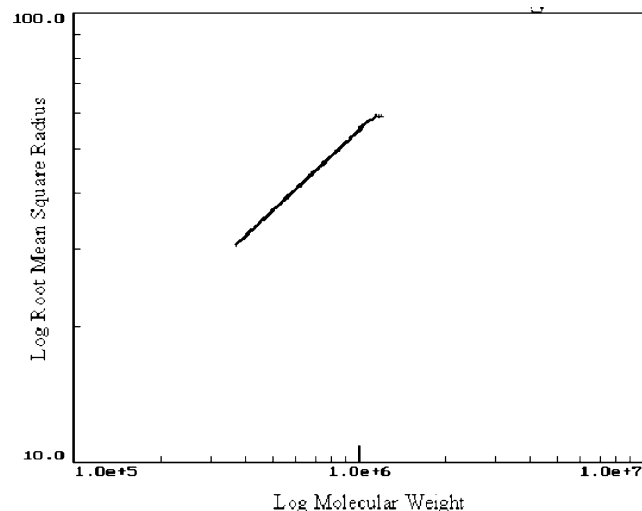


Fig. 6. The logarithmic RMS radius as a function of the logarithmic molecular weight of the original copolymer.

possible that the conformation stabilization depends on two chromophoric segment features, i.e. high molecular weight and the presence of Fc substituents. After 30 s of UV exposure the following behavior occurs: the $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ mass was greatly reduced, the copolymer molecular weight is still high, higher polydispersity is observed ($M_w/M_n = 2.4$), and the conformation is consistent with a semi-flexible polymer chain ($P = 0.75$). After 40 s of UV absorption the polydispersity decreased ($M_w/M_n = 1.3$) and the $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ forms more extended random coils ($P = 0.66$). Although the detailed conformation of the polysilane chain in solution is not completely known, a specific structure for the chromophoric segment was suggested by INDOS/S calculations. The results offered a simple MO explanation for the conformational dependence of polysilane chain excitation energy [11]. Thus, the polydispersity and molecular conformation behavior suggests that the processes involved in the photoreaction of $[(\text{FcMeSi})(\text{PhMeSi})_n]_m$ are considerably complicated. Further studies in these materials can be suggested in terms of longer copolymer irradiation periods of higher amounts of ferrocenyl substituents and clearly similar high molecular weight. The studies on these materials can be used in order to obtain a better understanding of the photo-physical properties because of their wide potential applications.

Acknowledgements

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References

- [1] J.E. Mark, H.R. Allock, R. West, *Inorganic Polymers*, Polymer Science and Engineering Series (Chapter 1), Prentice Hall, 1992 (Chapter 1).
- [2] M. Ozin, I. Manners, *Science* 287 (2000) 1460.
- [3] I. Manners, *Science* 294 (2000) 1664g.
- [4] K.H. Pannell, J.M. Rozell, J.M. Ziegler, *Macromolecules* 21 (1988) 276.
- [5] K.H. Pannell, J.M. Rozell, S. Vincenti, in: J.M. Ziegler, F.W. Gordon Fearon (Eds.), *Silicon-Based Polymer Science*, A Comprehensive Resource, Advances in Chemistry Series, vol. 224, 1990 (Chapter 20), American Chemical Society, Washington, D.C.
- [6] A. Díaz, M. Seymour, K.H. Pannell, J.M. Rozell, *J. Electrochem. Soc.* 137 (1990) 503.
- [7] J.A. Villegas, R. Olayo, J. Cervantes, *J. Inorg. Organomet. Polym.* 7 (1997) 51.
- [8] J.A. Villegas, R. Olayo, J. Cervantes, *J. Inorg. Organomet. Polym.* 8 (1998) 135.
- [9] A.R. Wolff, I. Nozue, J. Maxka, R. West, *J. Polym. Sci., Polym. Chem. Ed.* 26 (1988) 701.
- [10] R. West, *J. Organomet. Chem.* 300 (1986) 327.
- [11] K. Klingensmith, J.W. Downing, R.D. Miller, J. Michl, *J. Am. Chem. Soc.* 108 (1986) 7438.