

The Effects of Co-Solvents on the Reaction of Amino-Terminated Polystyrene with Fullerene

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ABSTRACT: Polymer tethered C_{60} fullerenes (PTFs) were synthesized by reacting amine terminated polystyrenes with fullerene under ambient conditions. While toluene was employed as the primary solvent in the synthesis, polar co-solvents were incorporated in various ratios to determine their effect on the reaction yield and nature of the product. The resultant PTFs were analyzed by GPC and UV-Vis spectroscopy to determine the number of adducts. The addition of a polar co-solvent was found to significantly affect the reaction rate, yield, and total number of substitutions on the fullerene. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Since their discovery¹ and synthesis in 1985,² fullerenes have been extensively researched for their unique chemical, physical, and electrical properties.³ Although some fullerenes such as nanotubes are relatively unreactive,⁴ C_{60} is very reactive largely due to the ring strain present in the cage structure.⁵ In fact, C_{60} behaves in most reactions like an electron deficient alkene. This ability to accept electrons has been utilized in a variety of applications ranging from “radical sponges” for biomedical applications^{6–10} to the predominant electron acceptor in most organic photovoltaics (OPVs).¹¹

Many types of reactions are possible with the C_{60} fullerene cage. In addition to oxidation and hydrogenations, C_{60} can be modified via radical coupling, pericyclic reactions, electrophilic additions, and nucleophilic additions.^{12,13} Some of the first modifications of fullerene were accomplished by the reaction of C_{60} with electron rich species such as Grignard reagents, alkyl lithium, and amines.¹² These reactions can be carried out with ease resulting in multiple additions to the fullerene cage. The reaction of primary and secondary amines, in particular, have been studied widely.^{14–19}

It was first believed that amine reactions proceeded via a simple nucleophilic addition mechanism resulting in a fullerene carbanion intermediate that would then be protonated as do the stronger nucleophiles such as Grignard and alkyl lithium reagents. Further studies, however, suggested that the process is, in fact, a single electron transfer (SET) process. This radical

nature was first suggested by Wudl et al.¹⁵ Using ESR, Wudl discovered that a significant number of radicals are present when C_{60} is mixed with a variety of amines.²⁰ Further spectroscopic evidence combined with observations that reaction rates are significantly reduced in the absence of light seems to confirm the radical nature of the process and suggests that the reaction proceeds via a single electron process from the amine to the fullerene creating a radical ion pair.¹⁷ Subsequent proton transfer and radical coupling results in the hydroamination product. Interestingly, it was noted that according to this mechanistic view, light may be required in non-polar solvents to increase the ability of fullerene to accept electrons.¹⁷ In fact, Weis et al. reported that the addition of 20% pyridine by volume as a polar co-solvent resulted in faster reaction rates.²¹ Using UV-Vis analysis, Weis et al. determined that the total time required for the reaction to come to completion was reduced by more than 50% in the presence of a polar co-solvent. However, neither this study nor any other has reported on the specific effects of solvent polarity on the addition of amines to C_{60} .

In this study, we have further explored the relationship between the nature of the solvent and the reaction of polymers containing terminal amines with C_{60} . A variety of co-solvents in varying concentrations were added to the reaction mixture. The nature of the mixed solvent was quantified using the Hildebrand solubility parameter (δ), which is the square root of the cohesive energy density.²² The reaction progress was followed using GPC coupled to a UV detector.

Table I. Summary of the PS-NH₂ Reactions and the Resulting Yields

Polymer M_w (g/mol)	Co-solvent	Percent co-solvent	Temperature (°C)	Reaction time (days)	Percent yield
1000	N/A	0	r.t.	10	22 ± 4
1000	Pyridine	10	r.t.	10	37
1000	Pyridine	20	r.t.	10	51 ± 7
1000	Pyridine	40	r.t.	10	73
1000	Pyridine	20	r.t.	3	25
1000	DMSO	20	r.t.	10	60 ± 4
1000	DMSO	20	r.t.	3	58
1000	DMSO	20	50	3	28
11000	N/A	0	r.t.	4	63
11000	Pyridine	20	r.t.	4	88
11000	DMSO	20	r.t.	4	85

EXPERIMENTAL

Materials

Fullerene C₆₀ (99.9+%) was purchased from M.E.R. Corporation (Tucson, AZ) and used without further purification. Amine terminated polystyrene (PS-NH₂) was purchased from Polymer Source (Montreal, Quebec) and used without further purification. Toluene, pyridine, dimethylformamide (DMF), and methyl sulfoxide (DMSO) were purchased from Aldrich Chemical and used without further purification.

Synthesis of PS-NH-C₆₀

Fullerene C₆₀ (30 mg, 41.6 μmol) was allowed to completely dissolve in 50 mL of toluene/co-solvent prior to the addition of 1100 MW PS-NH₂ (45.8 mg, 41.6 μmol). Reactions containing 20% co-solvent were performed at least two times to ensure repeatability. The reaction was allowed to proceed at room temperature for 10 days, after which time the product was precipitated in 150 mL methanol. The solids were isolated via vacuum filtration and allowed to completely dry before being added to 20 mL tetrahydrofuran. After vacuum filtering again to remove the unreacted fullerene, the THF filtrate containing the functionalized fullerene was retained and precipitated in 300 mL methanol. A final vacuum filtration yielded the polymer tethered fullerene (PTF), which was then characterized using gel-permeation chromatography.

Reaction Monitoring

Reaction progress was monitored during the course of the experiments via GPC to analyze the *in situ* formation of the adducted products. Extracts were taken at intervals and filtered through 0.45 μm filters. The samples were then injected on a Shimadzu 20-AT GPC with a Jordi DVB (1000 Å) column held at 40°C by a column oven. Elution of PTF was detected by a Shimadzu UV-Vis detector set at 335 nm. At this wavelength, only pure fullerene or products containing fullerene can be detected. The unmodified polymer does not absorb in this region. The observed polymer tethered fullerene peak contains a mixture of products. As a result, peak deconvolution was

performed using the peak fitting routine in IGOR Pro 6.0 (Wavemetrics).

RESULTS AND DISCUSSION

Results from all reactions can be found in Table I. The synthetic procedure was conducted using ~30 mg C₆₀ and a stoichiometric equivalent amount of polystyrene in 50 mL solvent. Initial experiments carried out in toluene were allowed to proceed for ten days. Following precipitation and subsequent removal of excess fullerene, the percent yield was found to be 22 ± 4%. GPC chromatograms indicated that the product consisted of a mixture of mono-, di-, and higher order adducts with the di-adduct being the major component as determined by peak deconvolution (Figure 1). The complex mixture of products is similar to those obtained by other groups with low molecular weight amines.¹⁷ The reactions of C₆₀ with PS-NH₂ generally produced products in lower yields possibly due to the steric hindrance of the polymer chain.

As mentioned previously, Weis et al.²¹ suggested that the use of pyridine as a co-solvent produced significantly faster reaction times. To confirm this observation, 20% (v/v) pyridine was added to the reaction mixture after dissolution of the fullerene and prior to the addition of PS-NH₂. The reaction was allowed

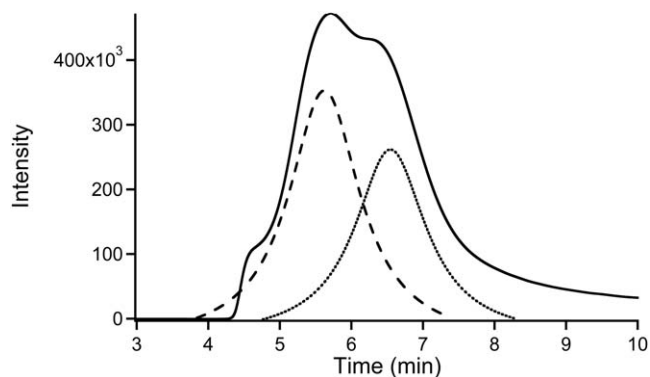


Figure 1. GPC chromatogram of PTF obtained from the stoichiometric reaction of C₆₀ with amine terminated polystyrene in toluene. Dashed lines are the calculated deconvoluted peaks for the di (---) and mono (- · -) products.

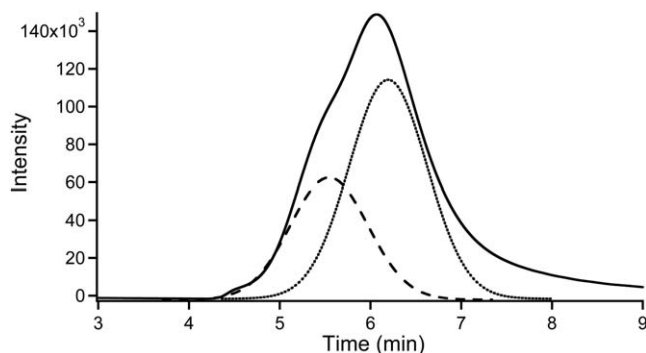


Figure 2. GPC chromatogram from a 1 : 1 fullerene : polystyrene reaction in toluene : pyridine (80 : 20). Dashed lines are the calculated deconvoluted peaks for the di (---) and mono (· · ·) products.

to proceed for 10 days and then worked up via the method described previously. The product yield with the addition of pyridine was $51 \pm 7\%$. The higher yield suggests that the reaction kinetics were improved significantly with the addition of a more polar co-solvent.

In addition to the increased product yield, GPC analysis indicated a shift toward a lower number of adducts, as shown in Figure 2. This was an unexpected and fortuitous result. It was expected that as the rate of reaction increased, the percentage of C_{60} with multiple adducts would also increase. This effect is currently being explored in further detail.

Although previous studies reported a solvent mixture containing 20% pyridine, it was unclear what effect increasing amounts of pyridine have on the reaction. Reactions containing various amounts of pyridine ranging from 10% to 40% were carried out in a similar manner to those described above. Figure 3 contains the percent yield data as a function of the concentration of pyridine. A significant increase in the mass of the recovered product is observed as the concentration of pyridine is increased. Concentrations higher than 40% were not achievable due to significantly decreased solubility of the fullerene in the reaction mixture.

Given the promising effect of pyridine as a co-solvent, the role of a co-solvent was further investigated with the addition of the

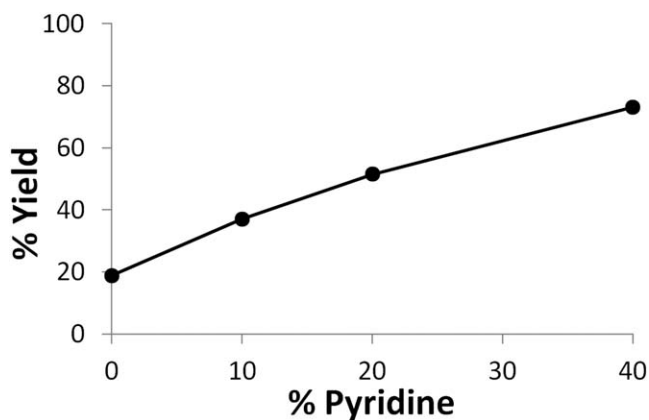


Figure 3. Graphical comparison of product yields using different volume fractions of pyridine in toluene.

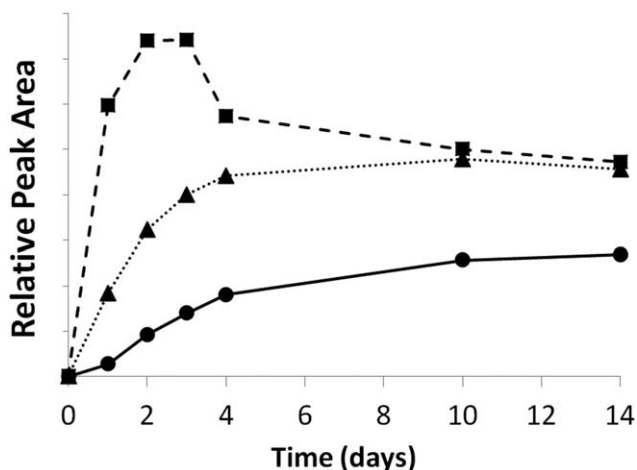


Figure 4. Peak area corresponding to product formation versus reaction time for no cosolvent (●), 20% pyridine (▲), and 20% DMSO (■).

more polar DMSO. The 20% DMSO reaction carried out for 10 days demonstrated only slight improvements over the pyridine reactions with the 20% DMSO reaction producing a yield of $60 \pm 4\%$ compared to $51 \pm 7\%$ for the 20% pyridine reaction. However, a significant color change from purple to brown is associated with the adduction of molecules to fullerene. This color change was observed much sooner in the reactions containing DMSO than with the previous reactions. Further investigation was performed by monitoring product formation as a function of time. Daily samples were taken and analyzed using GPC with a UV–Vis detector over the course of fourteen days. Plots of the relative peak area, which corresponds to the formation of PTF, versus time are shown in Figure 4. As expected, based on the previous yield data, the incorporation of pyridine significantly enhances the formation of PTF. For the toluene reaction, the maximum product formation occurs at approximately 10 days while for the toluene : pyridine reaction occurs at 10 days. This indicates that the co-solvent not only increases product formation, but it also alters the kinetics of the reaction. This is even more pronounced when DMSO is used as the co-solvent. As shown in Figure 4, DMSO dramatically speeds up both the kinetics of the reaction and the efficiency of the reaction. At 3 days, the amount of PTF in the reaction is significantly more than the other two reactions. In fact the percent yields at 3 days for the toluene, 20% pyridine, and the 20% DMSO were 12, 25, and 58% respectively.

While the incorporation of pyridine also appears to increase the amount of product formed, the addition of DMSO causes a significantly higher amount of product to be formed in a 3-day period, after which time some degradation begins to occur in the DMSO sample. This effect has been reported²³ and is thought to be the result of a oxidative process caused by light generated reactive oxygen species in solution. The nature of the decomposition products will be further explored in future studies. Based on these results, experiments were terminated after three days to compare yield and composition of the PTFs for the solvent/co-solvent solutions. The stacked chromatograms shown below in Figure 5 demonstrate the quantitative differences between the three syntheses.

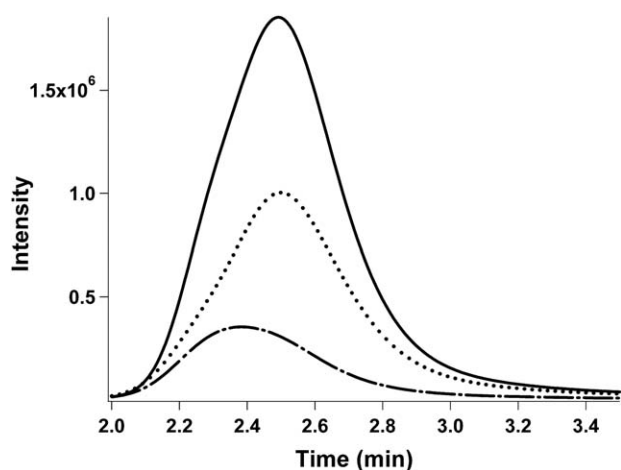


Figure 5. GPC chromatograms of the products in solution after 3 days for no co-solvent (---), 20% pyridine (· · ·), and 20% DMSO (—).

The collected product yields were found to be 12% with toluene, 25% with toluene : pyridine, and 58% when DMSO was used as a co-solvent. Deconvolution of the chromatogram peaks was performed using Igor Pro 6.0 software, the results of which indicated that DMSO was not only the fastest reaction with the highest percent yield, but also yielded product with a lower number of adducts. Yield and tether data are shown in Figure 6.

The significant differences between the results of the three reactions encouraged closer analysis as to the differences between the solvent(s). The Hildebrand Solubility Parameter (δ) for each solvent is represented in Table II. The δ is defined as the square root of the cohesive energy density and is typically used to determine solubility and interaction of solutes such as polymers in solvents. In the case of the mixed solvents, δ is calculated by determining the contribution of each solvent to the total solution. Values of δ for the mixed solvents used are also shown in Table II.

To confirm the correlation of δ and the percent yield, hexanes were also introduced as a co-solvent due to their low polarity. Hexanes have a δ of 7.24 which yields a value of 8.58 for the 80:20 toluene : hexanes solution. As expected,

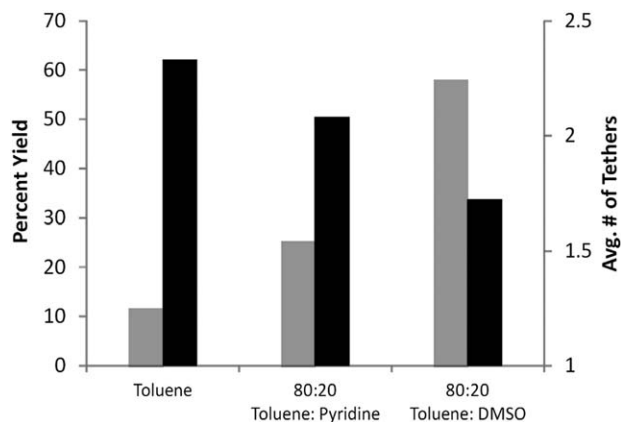


Figure 6. Summary of yield (gray) and of tether data (black) from 3-day reactions.

Table II. List of Hildebrand Solubility Values for the Solvents Used²⁴

Solvent	δ (cal ^{1/2} cm ^{3/2})
Hexane	7.24
Toluene : Hexane (80 : 20)	8.58
Toluene	8.91
Toluene : Pyridine (80 : 20)	9.25
Toluene : DMSO (80 : 20)	9.714
Pyridine	10.61
DMSO	12.93

the percent yield using that solvent mixture was reduced to 18.8% after 3 days of reaction. Although reaction yields provide some insight into the reaction, the rates of reaction can more clearly demonstrate the effect of co-solvents. Initial reaction rates were estimated using the difference in UV peak areas within the first day of the reaction since this difference is proportional to the number of moles formed within that time period. This initial rate was then plotted as a function of the δ of the reaction solution. This plot can be found in Figure 7. As shown in the plot, significant changes in reaction rate can be observed for relatively small changes in δ . Although reaction rates are expected to increase with increasing δ for the SET mechanism described previously, the polymeric nature of the reactant may also be affecting the reaction rates. Preliminary investigations using 11000 MW amine-terminated polystyrene have demonstrated higher yields (Table I), likely due to the higher weight fraction of the polymer. However, rates of reaction were not analyzed over the course of the higher molecular weight study. Alternate amine-terminated polymers and a range of polymer sizes will be investigated in future work to determine their effect on the hydroamination rates of C₆₀ in solvents of varied δ .

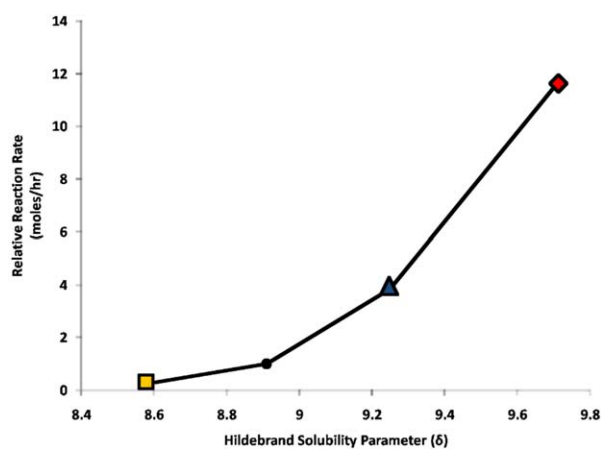


Figure 7. Plot of relative initial reaction rates versus HSP for reactions in toluene containing 20% hexane (■), no co-solvent (●), 20% pyridine (▲) and 20% DMSO (◆). (Line added to aid viewer's eye.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

From the findings of this study, it is evident that solvent polarity vastly affects both the rate at which the product is formed, and the amount of product formed during the synthesis. In fact, significant changes in the reaction rate and yield can result from relatively small changes in δ . Due to the SET nature of the reaction, a more polar solvent is expected to assist in the electron transfer process. However, due to the polymeric nature of the amine reactant, the effect of the solvent polarity may be even more pronounced than previously thought. It is well known that the nature of the solvent can significantly affect the size and shape of macromolecules which could significantly enhance or impede reactions based on steric factors as well as the position and availability of the polar end group. Further studies are planned to more accurately determine the effects of δ on the reaction of other amine terminated polymers with C₆₀.

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REFERENCES

- Sumio, I. *J. Cryst. Growth* **1980**, *50*, 675.
- Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
- Prato, M. *J. Mater. Chem.* **1997**, *7*.
- Niyogi, S.; Hamon, M. A.; Hu, H.; Zhao, B.; Bhowmik, P.; Sen, R.; Itkis, M. E.; Haddon, R. C. *Acc. Chem. Res.* **2002**, *35*, 1105.
- Haddon, R. C. *Acc. Chem. Res.* **1992**, *25*, 127.
- Markovic, Z.; Trajkovic, V. *Biomaterials* **2008**, *29*, 3561.
- Partha, R.; Conyers, J. L. *Int. J. Nanomed.* **2009**, *4*, 261.
- Yin, J. J.; Lao, F.; Fu, P. P.; Wamer, W. G.; Zhao, Y. L.; Wang, P. C.; Qiu, Y.; Sun, B. Y.; Xing, G. M.; Dong, J. Q.; Liang, X. J.; Chen, C. Y. *Biomaterials* **2009**, *30*, 611.
- Bosi, S.; Da Ros, T.; Spalluto, G.; Prato, M. *Eur. J. Med. Chem.* **2003**, *38*, 913.
- Friedman, S. H.; Decamp, D. L.; Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506.
- Thompson, B. C.; Frechet, J. M. J. *Angew. Chem. Int. Ed.* **2008**, *47*, 58.
- Hirsch, A. *Angew. Chem. Int. Ed. Eng.* **1993**, *32*, 1138.
- Hirsch, A. *Synthesis* **1995**, 895.
- Geckeler, K. E.; Arsalani, N. *Fullerene Sci. Technol.* **1997**, *5*, 127.
- Hirsch, A.; Li, Q.; Wudl, F. *Angew. Chem. Int. Ed. Eng.* **1991**, *30*, 1309.
- Hwu, J. R.; Kuo, T. Y.; Chang, T. M.; Patel, H. V.; Yong, K. T. *Fullerene Sci. Technol.* **1996**, *4*, 407.
- Miller, G. P. *Comptes Rendus Chimie* **2006**, *9*, 952.
- Miller, G. P.; Millar, J. M.; Liang, B. M.; Uldrich, S.; Johnston, J. E. *J. Chem. Soc. Chem. Commun.* **1993**, 897.
- Schick, G.; Kampe, K. D.; Hirsch, A. *J. Chem. Soc. Chem. Commun.* **1995**, 2023.
- Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P. M.; Koch, A.; Eckert, H.; Srdanov, G.; Webb, H. M. *ACS Symp. Ser.* **1992**, *481*, 161.
- Weis, C.; Friedrich, C.; Mulhaupt, R.; Frey, H. *Macromolecules* **1995**, *28*, 403.
- Burke, J. *The Book and Paper Group ANNUAL*, **1984**.
- Isobe, H.; Tanaka, T.; Nakanishi, W.; Lemiegre, L.; Nakamura, E. *J. Org. Chem.* **2005**, *70*, 4826.
- Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, *97*, 3379.