Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Surface Properties of Polybutadiene Chains End-Capped with Two Types of Fluorosilicon Groups

D. V. Patwardhan[a]; H. Zimmer[a]; J. E. Mark[a]
[a] Department of Chemistry and the Polymer Research Center, The University of Cincinnati Cincinnati,

To cite this Article Patwardhan, D. V. , Zimmer, H. and Mark, J. E.(1998) 'Synthesis and Surface Properties of Polybutadiene Chains End-Capped with Two Types of Fluorosilicon Groups', Journal of Macromolecular Science, Part A, 35: 12, 1941 — 1955

To link to this Article: DOI: 10.1080/10601329808000989

URL: http://dx.doi.org/10.1080/10601329808000989

J.M.S.—PURE APPL. CHEM., A35(12), pp. 1941–1955 (1998)

SYNTHESIS AND SURFACE PROPERTIES OF POLYBUTADIENE CHAINS END-CAPPED WITH TWO TYPES OF FLUOROSILICON GROUPS

D. V. Patwardhan*, H. Zimmer, and J. E. Mark†
Department of Chemistry
and the Polymer Research Center
The University of Cincinnati
Cincinnati, OH 45221-0172

Key Words: Polybutadiene, Fluorosilicon Groups, Segregation, Surface Tensions

ABSTRACT

Polybutadiene diol chains were end-capped, using two highly fluorinated monochlorosilanes, specifically di(4-fluorophenyl)-methylchlorosilane and di[3,5-bis(trifluoromethyl)phenyl]methylchlorosilane. The resulting chains, with one and three fluorine atoms at their ends, respectively, were characterized using contact angle measurements, X-ray photoelectron spectroscopy (XPS), and Time-of-flight secondary ionization mass spectroscopy (TOFSIMS). The observed lowered surface tensions and results from the chemical analyses were consistent with migration of the fluorosilicon end groups to the polymer surfaces.

INTRODUCTION

Fluorosilioxane polymers are an interesting and useful class of materials due to their unique properties such as low surface tension, low coefficient of

---

*Present address: Chromatix Separation Sciences, 91 Church Street, Sutter Creek, CA 95685.

†markje@email.uc.edu, http://jemcom.crs.uc.edu/.

friction, non-flammability, and solvent and chemical resistances. An example of an important polymer in this class is poly(3,3,3-trifluoropropylmethylsiloxane), a commercially available fluorosilicon polymer which is particularly resistant to acids and bases [1].

Two limitations to commercialization of these fluorosiloxane polymers are the relatively high costs of the starting materials, and difficulties in using current processing technologies [2]. They are, nonetheless, of considerable interest because the fluorine or silicon atoms present in their repeat units give them the very attractive properties mentioned. It is possible to achieve these desired properties at much lower contents of Si or F atoms, however, by exploiting the ability of silicon-containing groups to migrate to the surfaces of a polymer. For example, Gaines and his co-workers carried out studies of polydimethylsiloxane-co-polystyrene block copolymer in the 1970s that showed that even if the polydimethylsiloxane (PDMS) were present in low concentrations (0.05-5 wt%), the polymer surface nonetheless appeared to be almost entirely siloxane [3], with its celebrated lubricity. They measured contact angles with change in percent siloxane and found that they approached siloxane-like values ($\approx 100^{o}$) even at concentrations as low as 0.2%! Similarly, fluorine-containing additives have been mixed into commercially available polymers to modify their surfaces [4]. The drawback of this method of surface modification is that, typically, the parent polymer and the additives are sufficiently different to undergo macroscopic phase separation.

Since the early work by Gaines and his coworkers, a great deal of work has been done with block copolymer systems with one of the constituent sequences being a polysiloxane [5-10]. The polysiloxane sequences in such polymers migrate to the surface, thus healing the surface after abrasion, or other type of erosion during their use. Because of their abilities to generate or restore surface properties that are very different from that of the bulk material, these systems have been called "smart polymers" or "self-healing systems". Their being copolymers, with chemical bonds between the two components, gives them much better stability than the corresponding blends.

One extension of this idea is the concept that an excess of a low surface tension fluorine moiety can act as a "reservoir" for its continual transport to a polymer surface. For example, Ober *et al.* modified commercially available styrene-isoprene block co-polymers with "short fingers" of perfluorylalkyl or dimethylsiloxy groups [11, 12]. When these copolymers were mixed with styrene homopolymers, they exhibited surface segregation of the low surface tension moiety. The behavior and the amount of migration of the low surface energy sequences depended on the molecular weight of the polymer, and on the processing conditions, as expected.

End groups on a polymer chain can show a similar tendency to migrate to a surface [13-22]. For example, DeSimone and his coworkers have shown that perfluoro-alkyl-terminated polymers exhibit surface segregation of the fluorosilicon end groups. In this study, styrene was polymerized with an anionic catalyst, and the living anionic polymer chains were terminated with a chlorosilane which contained perfluoroalkyl groups [14, 15]. The fact that these end groups have lower surface tensions than the main chain caused them to migrate to the surfaces of the polymer. At around the same time, Koberstein *et al.* carried out investigations in which the interfacial tensions between two polymers was correlated with the natures of their end groups [16-21]. They studied blends of PDMS and poly(butadiene) (PBD), and varied the interfacial tension by varying the nature of the end groups and their number (through changes in the molecular weight of the PDMS). They observed changes in interfacial tension from migration of PDMS groups to the surfaces, and this depended, as expected, on both the nature of end groups and their number density.

In all the examples mentioned, the common link is low surface tension blocks or end groups play a very important role in the determination of the surface properties by migrating to the polymer surface. The force for this migration is the difference in the surface free energy between the blocks in a block copolymer or between the end groups and the main chain in the case of a homopolymer.

The polymer chosen for the present study was polybutadiene diol (i.e., hydroxyl terminated polybutadiene), with the intention of capping it with siloxy end groups. The unmodified PBD has the advantage on not containing any silicon, thus simplifying identification of any observed silicon as coming from the subsequently added end groups. This polymer also has a double bond which can be utilized to crosslink the sample, which is necessary for the planned contact angle measurements. Its being hydroxyl terminated facilitates reactions with two fluorinated monochlorosilanes chosen to introduce end groups having much lower surface tensions than PBD itself.

EXPERIMENTAL

Materials

Two PBD diols were obtained as samples from the Elf Atochem Company. They consisted of 56.6% *trans*, 15.1% *cis*, and 28.3% vinyl units, and had weight-average molecular weights M_w of 6200 and 2500 g/mol. Methyltrichlorosilane, 4-fluoro-1-bromobenzene, and 3,5-bis(trifluoro-methyl)bromobenzene, and dicumyl peroxide were purchased from the Aldrich Chemical Company and used as received. Samples of *t*-BuLi and *sec*-BuLi were kindly donated by the FMC Corporation, and diethylether was obtained from the Fisher Scientific Company in Sure Seal™ bottles (with a freshly opened bottle used for every organolithium reaction). Methanol, tetrahydrofuran (THF), and sterilized glass slides were also purchased from Fisher, and silica gel from Merck. All were used as received [23].

Syntheses of the Chlorosilanes

The reactions for the synthesis of the first chlorosilane, di(4-fluorophenyl)-methylchlorosilane, are shown in Figure 1. They were carried out in a 500 ml, three-neck round-bottom flask, which had been flame dried and flushed with argon. The flask was equipped with a stirring bar and a dropping funnel through which 6.46 ml of *sec*-BuLi and 200 ml each of pentane and diethylether were added. After the addition was complete, the mixture was cooled to -100°C with liquid nitrogen. An amount of 17.5 g (0.1 mole) of 1-bromo-4-fluorobenzene was then added dropwise to the flask with a syringe over a period of 30 minutes. The reaction mixture was then warmed to room temperature with continuous vigorous stirring. An amount of 5.85 ml (0.05 moles) of methyltrichlorosilane was added to another three-neck flask containing 200 ml of diethylether. The lithium compound prepared in the first flask was added to it through a canula over a period of 30 minutes. After the addition was completed, the mixture was reacted for an additional 24 hours, during which the lithium salts precipitated. The mixture was then filtered to remove salts, and the diethylether and pentane were evaporated to yield an amber colored reaction product. It was then distilled under vacuum (0.1 mm of mercury, 150°C) to give pure di(4-fluorophenyl)methylchlorosilane as a colorless liquid. The monomer was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy [23].

The reactions for the formation of the second chlorosilane, di[3,5-bis(trifluoromethyl)phenyl]methylchlorosilane, are shown in Figure 2. The procedures were the same as those used for the first chlorosilane, except for the use of 5.97 ml of *t*-BuLi and 1.76 ml (0.01 moles) of 3,5-bis(trifluoromethyl)-bromobenzene. The pure compound was obtained as a colorless liquid after distillation, and was also characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy.

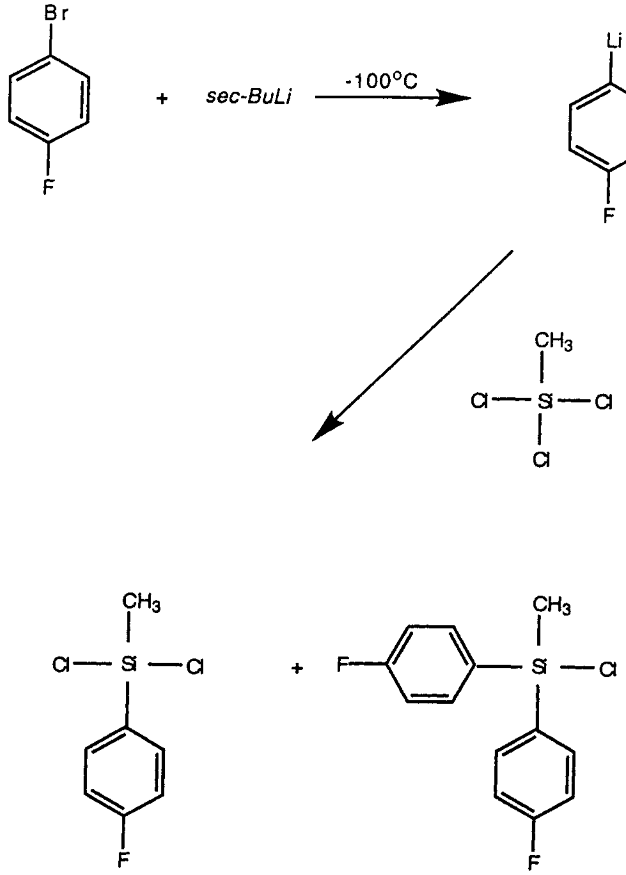

Figure 1. Synthesis of di(4-fluorophenyl)methylchlorosilane.

End-Capping of the Polybutadiene Diols

In the case of the di(4-fluorophenyl)methylchlorosilane), a stirring bar was placed into a 500 ml, three-neck round-bottom flask which had been flame dried and flushed with argon. 5 g of one of the two polybutadiene diols, and 1.0 ml pyridine were placed into the flask, along with 50 ml of THF. The requisite amount of freshly-distilled monochlorosilane (0.39 g of chlorosilane per g of polymer for $M_w = 6200$, 1.012 g of chlorosilane per g of polymer for $M_w = 2500$ g mol^{-1}) was added to the flask using an oven-dried syringe under a stream of argon. A colorless precipitate was seen forming almost immediately, indicating that the end capping of the chains was rapid. The reaction mixture was stirred for

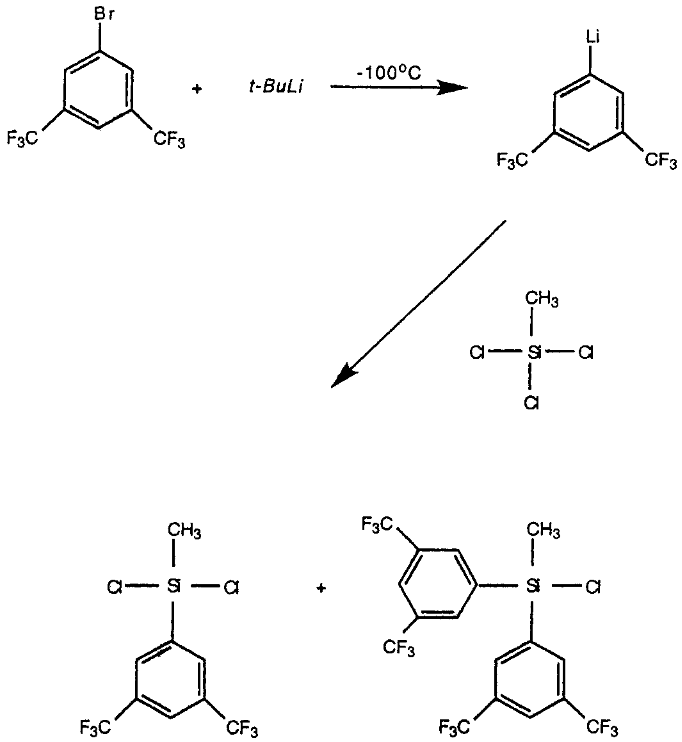

Figure 2. Synthesis of di(3,5-bis(trifluoromethyl)phenyl)methylchloro-silane.

two more hours and then filtered through silica gel. Since some of the end-capped polymer could have undergone hydrolysis at the C–O–Si ends during these synthetic procedures, it extensively washed with methanol to remove any low molecular weight materials. Since the resulting di(4-fluorophenyl)methylsilane-terminated polybutadiene contains two fluorine atoms per chain, it was designated the "2F" polymer, and was characterized by FTIR spectroscopy [23].

In the case of capping with the di[3,5-bis(trifluoromethyl)-phenyl]methylchlorosilane, the procedure was similar to that for the 2F polymer. The difference was in the amount of monochlorosilane used (0.212 g of chlorosilane per g of polymer for M_w = 6200, and 0.535 g of chlorosilane per g of polymer for M_w = 2500). The resulting end-capped polymer, designated "6F", was also characterized by FTIR spectroscopy.

Characterization

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopic determinations were performed on a Bruker 250 instrument. $CDCl_3$ was used as the solvent and referenced to TMS at 0 ppm. The FTIR spectra were obtained using a Perkin-Elmer model 1600, and Gel Permeation Chromatography (GPC) was performed on a Waters 599 high pressure chromatograph fitted with 500 Å, 10^3 Å, and 10^4 Å Ultrastyragel columns. The GPC detection system was a differential refractometer, commercially known as Waters 410 unit, with spectroscopic grade toluene as the solvent. The instrument was calibrated against PDMS and polystyrene standards.

Surface properties of these materials were determined using contact angle measurements. Since the surface properties of a polymer are very sensitive to small amount of impurities, extensive purification of the end-capped polymer was carried out. In the present case, the most likely impurities would be excess monochlorosilane, pyridine, and the two corresponding silanols di(4-fluorophenyl)methylsilanol and di[3,5-bis(trifluoromethyl)-phenyl]methylsilanol. The excess chlorosilane was trapped by silica gel, and other possible impurities were removed by re-precipitation of the polymer into methanol. The contact angle measurement were carried out on networks of the 2F and 6F polymers prepared using dicumyl peroxide as the crosslinking agent. The polymer and peroxide were thoroughly mixed and then drawn out on a glass slide to films which were cured at 160°C for two hours. They were then cooled to room temperature and rinsed with methanol [23].

Values of the surface tension were determined by measuring contact angles on the polymer surface for de-ionized ultra-pure water and methylene iodide (CH_2I_2). A syringe was used to place a single drop of the test liquid onto a previously unwetted surface of the polymer film on a glass slide. The droplet was allowed to stand for 15 seconds, and the contact angles then measured using a Video Contact Angle System and VCA_{2000} instrument. Six contact angles were measured for each solvent on a given polymer surface, and three samples of each polymer were investigated. All contact angles were measured at room temperature, and should be accurate to ± 4°.

The contact angle data were used to determine solid surface tensions for the un-capped and end-capped polymers, using the geometric mean technique as described by Owens and Wendt [24]. The relevant equation is :

$$\frac{\sigma_1(1+\cos\theta)}{2\left(\sigma_1^d\right)^{\frac{1}{2}}} = \left(\sigma_2^d\right)^{\frac{1}{2}} + \left(\sigma_2^p\right)^{\frac{1}{2}}\left(\frac{\sigma_1^p}{\sigma_1^d}\right)^{\frac{1}{2}} \qquad (1)$$

where θ is the contact angle and σ represents the surface tension. The superscript d refers to the dispersion force component of the surface tension, and the superscript p refers to the polar component. The dispersive and polar components of the surface tension at 23°C for the test liquids have been reported to be $\sigma_l^d = 21.7$ mN/m and $\sigma_l^p = 50.8$ mN/m for water, and as $\sigma_l^d = 48.1$ mN/m and $\sigma_l^p = 1.3$ mN/m for CH_2I_2 [24].

Angle-dependent X-ray photoelectron (XPS) spectra were obtained on a Physical Electronics 5300 instrument, with 300 watts Mg Kα radiation as the excitation source. The pass energy was 44.75 eV and 17.90 eV, and peak deconvolution was achieved using an Apollo computer running a standard Perkin-Elmer software package. The polymer was deposited on a 1 cm x 1 cm clean, scratchless, stainless steel plate, and then rinsed with methanol just prior to use. The sample depth analyzed ranged from approximately 20 to 90Å [23].

Time-of-flight Secondary Ionization Mass Spectroscopy (TOFSIMS) was carried out on a Kratos PRISM instrument at the Armco Research and Technology Center. It was equipped with a reflectron type time-of-flight mass analyzer and a 25 KV liquid metal source of 69 Ga^+ ions with a minimum beam size of 500 Å. A pulse width of 10-50 ns and a total integrated ion dose of about 1011 ions/cm^2 were used to obtain positive and negative spectra. The samples were prepared as for the XPS measurements, and the depth of analysis was approximately 5 Å.

Other end-group characterization techniques such as titration were not useful, since fluorosilicon end groups are difficult to titrate. Also the increases in molecular weight from the chain ends are so small that GPC was not very informative.

RESULTS AND DISCUSSION

Structures of the Chlorosilanes

As expected, di(4-fluorophenyl)methylchlorosilane and di[3,5-(trifluoromethyl)phenyl]methylchlorosilane were the major products in their respective reactions because, after addition of the first fluorine moiety at the silicon center, the remaining Si-Cl bonds become more activated. This is due to the electronegative nature of fluorine, which facilitates the addition of a second phenyl substituent.

The NMR spectra of the di(4-fluorophenyl)methylchlorosilane gave the following results [23]:

^1H NMR (ppm): 0.9 (1H, s), 7.1(2H, m), 7.65(2H, m).
^{13}C NMR (ppm): 1.079, 115.4(d), 129.9(s), 136.1(d), 162.5(d).

The ^{1}H spectrum shows a peak at 0.9 ppm for the methyl groups and two peaks at 7.10 and 7.60 ppm due to the aromatic protons. The integration for both gives 3:8, as expected (for two phenyls substituted at the silicon center). The ^{13}C spectrum also shows a peak at 1.09 ppm for the methyl group, and a complex pattern between 100 and 160 ppm attributed to the phenyl group.

The NMR spectra of the di[3,5-bis(trifluoromethyl)phenyl]methylchlorosilane gave the following results:

^{1}H NMR(ppm): 1.1 (3H, s), 8.0-8.1(3H, m).
^{13}C NMR (ppm): 0.22, 116.8, 121.1, 125.4, 129.8, 132.4, 133.8, 135.9.

The ^{1}H spectrum showed a peak at 1.0 ppm for the methyl groups, and two peaks at 7.9-8.0 ppm from the aromatic protons. The integration for both gave 1:2, as expected, for two phenyls at the silicon. The ^{13}C spectrum showed a peak at 0.0 ppm for the methyl groups, and a pattern between 100 and 160 ppm for the phenyl groups.

Structures of the End-Capped Polymers

In the case of the "2F" polymer, the spectroscopic results are summarized by:

FTIR (cm^{-1}): 3075, 3015, 2895, 2848, 1651, 1597, 1504, 1444, 1358, 1311, 1245, 1165, 1112, 972, 832, 728.

For the "6F" polymer, they were:

FTIR (cm^{-1}): 3086, 3018, 2919, 1647, 1462, 1375, 1285, 1190, 1147, 1103, 970, 918, 832, 782, 708, 684.

For both the end groups and both polymer molecular weights, the infrared spectra confirmed the completion of the end-capping reaction by the absence of an -OH peak around 3300 cm^{-1}. Since the derivatization of the polymers occurred only on the chain ends, the ^{1}H-NMR and ^{13}C-NMR spectra did not provide any significant characterization information.

Surface Properties

The contact angles for the un-capped and the end-capped polymers, for both the molecular weights, and for both the chlorosilanes as end groups are given in Table 1. Also included are values of the surface tension calculated from the contact angles with the methylene iodide. Several important comparisons can be drawn from this table:

TABLE 1. Contact Angles and Surface Tensions

M (g mol^{-1})	Polymer	Contact angles H_2O	Contact angles CH_2I_2	Surface tension (mN/m) X10^3
6,200	Uncapped	72.	43.	1.65
	2F ends	96.	73.	0.80
	6F ends	96.	76.	0.75
2,500	Uncapped	60.	40.	1.75
	2F ends	101.	74.	0.75
	6F ends	86.	65.	1.01

a. The contact angles of the fluorosilicon end-capped polymers are higher than those of the uncapped polymers, with correspondingly lower surface tensions, as expected. This is presumably due to enrichment of the end groups at the surfaces.

b. In some cases, the differences in the contact angles between the uncapped and end-capped polymers are more pronounced for the 4-fluorophenyl end caps. This could be due to the different orientation effects of the two end groups at the polymer surface, possibly resulting from the greater compactness of the 4-fluorophenyl group or the smaller number of fluorine atoms it contains.

Elemental Compositions by XPS

Table 2 gives the elemental concentrations for the bulk materials and their surfaces at three depths, for the two molecular weights of the polymer, and the two end groups. These results suggest that:

a. The percentages of silicon and fluorine at depths ranging from 20-90 Å are generally significantly higher than would be expected from homo-

TABLE 2. Elemental Distributions from X-ray Photoelectron Spectroscopy

M_w (g mol^{-1})	Polymer	Element	Bulk	20 Å	70 Å	90 Å
6,200	2F	C	86.6	66.3	74.9	79.3
		Si	0.91	13.2	8.48	6.46
		F	1.23	1.07	0.85	0.90
		O	0.51	19.6	16.0	13.4
	6F	C	82.0	63.7	67.8	73.5
		Si	0.84	3.15	1.96	1.96
		F	6.89	19.5	15.3	14.3
		O	1.13	12.1	13.7	12.5
2,500	2F	C	83.3	74.8	83.4	85.5
		Si	1.82	9.52	5.50	4.18
		F	2.46	1.86	2.70	2.53
		O	1.02	13.9	8.38	7.80
	6F	C	74.2	65.7	69.6	74.5
		Si	1.71	4.65	3.27	2.23
		F	14.0	18.3	14.1	12.7
		O	1.96	11.3	12.9	10.5

• Remainder is hydrogen.

geneity (i.e., there is migration of the end groups to the surfaces). Since the end groups are attached through oxygen atoms their concentrations are also generally higher at the surfaces. Since most of the carbon is in the polymer backbone, its concentrations at thesurfaces are correspondingly decreased.

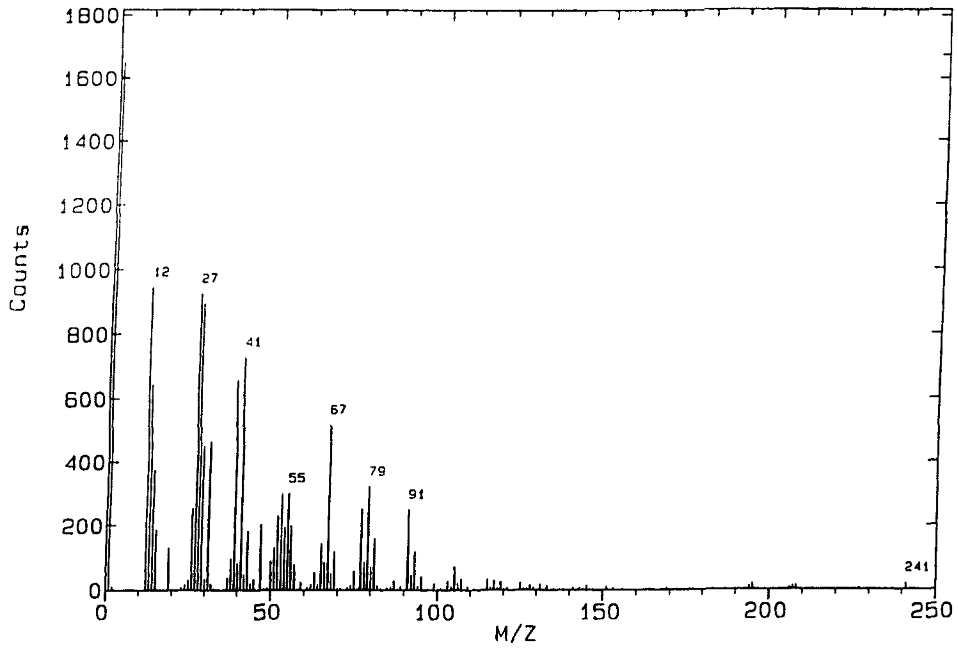

Figure 3. Positive TOFSIMS spectrum of di(3,5-bis(trifluoromethyl)phenyl)-methylchlorosilane terminated polymer.

b. The differences between the observed and expected concentrations of silicon and fluorine generally decrease with increasing depth (less segregation occurs further from the surface) [22].

c. In the case of the 2F polymer, with 4-fluorophenyl groups, the percentage of silicon at a depth of 20 Å is as much as fourteen times that expected from homogeneity. The fluorine concentrations, however, show less definitive trends.

d. In contrast, in the case of the 6F polymer, with 3,5-bis(trifluoromethyl)phenyl groups, the percentage of silicon at a depth of 20 Å is at most only three or four times greater than that expected from homogeneity.

The comparisons given in parts c and d are consistent with the contact angle values for the lower molecular weight polymer, with its higher number

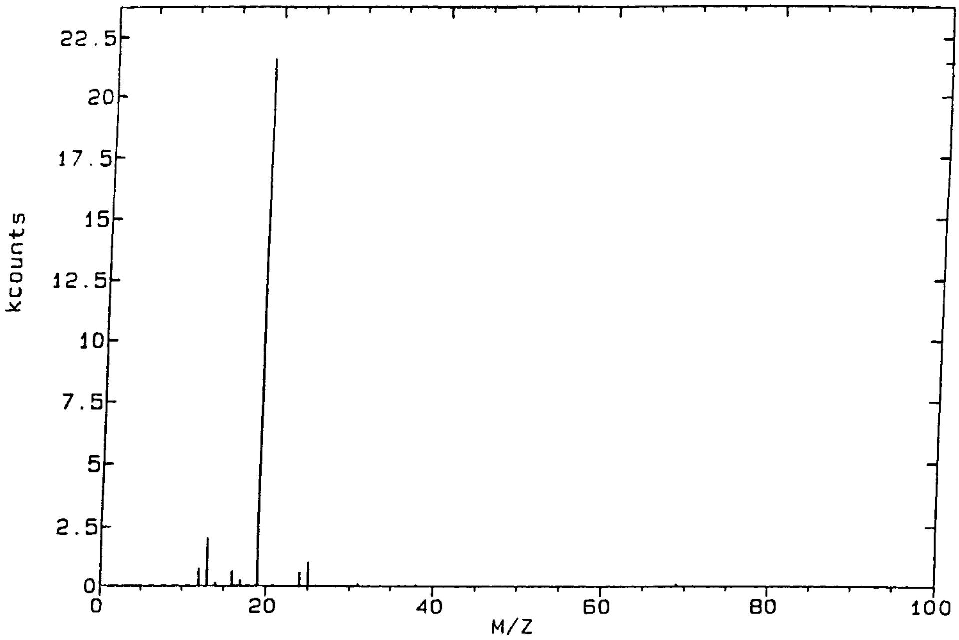

Figure 4. Negative TOFSIMS spectrum of di(3,5-bis(trifluoromethyl)phenyl)-methylchlorosilane terminated polymer.

density of end groups. The contact angles are seen to be increased more from the 4-fluorophenyl end group than for the 3,5-bis(trifluoromethyl)phenyl group, and both were substantially higher than those of the un-capped polymer.

Elemental Compositions by Time of Flight Secondary Ionization Mass Spectroscopy

Examples of TOFSIMS results for the higher molecular 6F polymer are shown in Figures 3 and 4. There seems to be a significant peak for fluorine at 19 amu in the negative spectrum and for silicon at 28 amu in the positive spectrum. Both were absent in the spectrum for the uncapped polymer. The absence of a peak at 73 amu for the trimethylsilyl group [-Si$(CH_3)_3$] is important, since it would have indicated the presence of small amounts of ubiquitous low molecular weight siloxanes, which can change the surface properties significantly. Thus, these TOFSIMS results are also consistent with the migration of the fluorosilicon end groups to the surface.

CONCLUSION

Synthesis of two highly fluorinated chlorosilanes was achieved, and used to introduce surface-active end groups on polybutadiene. Several techniques established the segregation of the end groups to the surfaces of the polymers. Some observed differences in segregation could be due to different orientations of the end groups related to structural features such as their sizes and numbers of fluorine atoms.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Grant DMR-9422223 (Polymers Program, Division of Materials Research), and to thank Armco Research and Technology for their help with the TOFSIMS measurements.

REFERENCES

[1] M. J. Owen, in *Siloxane Polymers,* S. J. Clarson and J. A. Semlyen, Eds., Prentice Hall, Englewood Cliffs, New Jersey, 1993.

[2] M. J. Owen and H. Kobayashi, *Trends in Polymer Science*, *3*, 330 (1995).

[3] G. L. Gaines, Jr. and G. W. Bender, *Macromolecules*, *5*, 82 (1971).

[4] A. Nobuo and S. Shinichiro, European Patent #481794 (1990).

[5] A. Noshay and J. E. McGrath, *Block Copolymers: Overview and Critical Survey*; Academic Press, New York, 1977.

[6] S. J. Clarson, S. D. Smith, C. E. Selby, J. O. Stuart, W. van Ooij, A. Sabata, and N. Cave, *Journal of Inorg. Organometallic Polymers*, *4*, 85 (1994).

[7] S. J. Clarson, J. O. Stuart, C. E. Selby, A. Sabata, S. D. Smith, and A. Ashraf, *Macromolecules*, *28*, 674 (1995).

[8] X. K. Zhang, J. O. Stuart, S. J. Clarson, A. Sabata, G. Beaucage, *Macromolecules*, *27*, 5229 (1994).

[9] K. Senshu, T. Furuzono, N. Koshizaki, S. Yamashita, T. Matsumoto, A. Kishida, and M. Akashi, *Macromolecules*, *30*, 4421 (1997).

[10] N. Furukawa, Y. Yamada, M. Furukawa, M. Yuasa, and Y. Kimura, *J. Polym. Sci., Polym. Chem.*, *35*, 2239 (1997).

[11] S. S. Hwang, C. K. Ober, S. Perutz, D. R. Iyengar, B. Schneggenburger, and E. J. Kramer, *Polymer*, *36*, 1321 (1995).

[12] D. R. Iyengar, M. Perutz, C. Dai, C. K. Ober, and E. J. Kramer, *Macromolecules*, *29*, 1229 (1996).

[13] W. Zhao, X. Zhao, M. H. Rafailovich, J. Sokolov, R. J. Composto, S. D. Smith, M. Satkowski, T. P. Russell, W. D. Dozier, and T. Mansfield, *Macromolecules*, *26*, 561 (1993).

[14] M. O. Hunt, A. M. Belu, R. W. Linton, and J. M. DeSimone, *Macromolecules*, *26*, 4854 (1993).

[15] M. O. Hunt, A. M. Belu, R. W. Linton, and J. M. DeSimone, *Macromolecules*, *27*, 1905 (1994).

[16] S. H. Anastasiadis, I. Gancarz, and J. T. Koberstein, *Macromolecules*, *21*, 2980 (1988).

[17] S. H. Anastasidis, I. Gancarz, J. T. Koberstein, *Macromolecules*, *22*, 449 (1989).

[18] C. A. Fleischer, J. T. Koberstein, V. Krukonis, and P. A. Wermore, *Macromolecules*, *26*, 4172 (1993).

[19] C. Jalbert, J. T. Koberstein, I. Yilgor, P. Gallagher, and V. Krukonis, *Macromolecules*, *26*, 3069 (1993).

[20] C. A. Fleischer, A. R. Morales, and J. T. Koberstein, *Macromolecules*, *27*, 379 (1994).

[21] J. F. Elman, B. D. Johs, T. E. Long, J. T. Koberstein, *Macromolecules*, *27*, 5341 (1994).

[22] J. Wen, G. Samorjai, F. Lim, and R. Ward, *Macromolecules*, *30*, 7206 (1997), and relevant references cited therein.

[23] D. V. Patwardhan, Ph. D. Thesis in Chemistry, The University of Cincinnati, 1996.

[24] M. J. Owen and R. C. Wendt, *J. Appl. Polym. Sci.*, *13*, 1741 (1969).

Received April 10, 1998
Revision received July 25, 1998