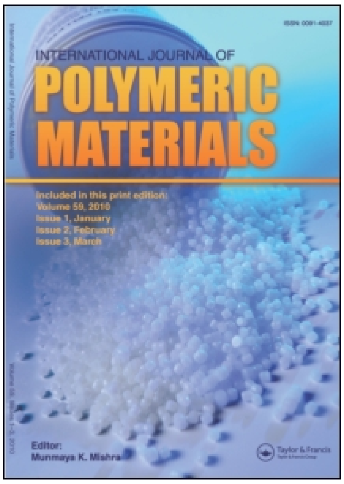

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Tadashi Narita[a]
[a] Department of Environmental Engineering, Saitama Institute of Technology, Saitama, Japan

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Silicon or Fluorine-Containing Polymers

TADASHI NARITA

Department of Environmental Engineering, Saitama Institute of Technology, 1690 Fusaiji, Okabe-machi, Osato-gun, Saitama 369-02, Japan

The study of silicon- and fluorine-containing polymers are of interest from both an academic and industrial perspectives as functional materials of high performance. Intensive research work on syntheses and characterizations of these polymers were presented at various meetings and symposiums sponsored by the Society of Polymer Science, Japan (SPSJ).

In this chapter, the papers presented in the special symposium entitled "Silicon or Fluorine-containing Polymers" organized by Prof. Kawakami (1980) at the 39th Annual Fall Meeting of SPSJ in Nagoya are reviewed. The review is focused mainly on syntheses of new silicon- and fluorine-containing polymers.

SILICON-CONTAINING POLYMERS

Silicon-containing polymers are generally synthesized in order to prepare gas-permeable or pervaporation membranes. Many papers on syntheses of several silicon-containing polymers were reported.

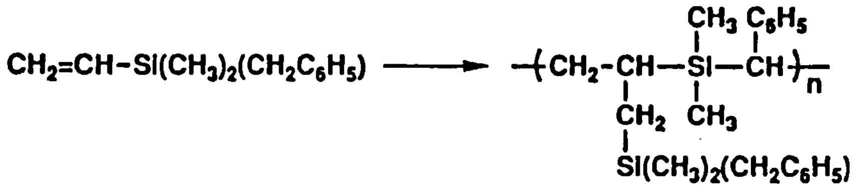
S. Nakahama and his coworkers previously reported the anionic living polymerization of silicon-containing vinyl monomers. They examined the anionic polymerization reactivity of *para*-substituted styrene derivatives such as $CH_2{=}CH{-}C_6H_4{-}Si(OCH_3)(CH_3)_2$, $CH_2{=}CH{-}C_6H_4{-}Si(OC_2H_5)(CH_3)_2$, $CH_2{=}CH{-}C_6H_4{-}Si(O\text{-}iso\text{-}C_3H_7)(CH_3)_2$ and $CH_2{=}CH{-}C_6H_4{-}Si(O\text{-}tert\text{-}C[_4H_9)(CH_3)_2$, and butadiene derivatives such as $CH_2{=}CH{-}C(Si(OCH_3)_3){=}CH_2$ and $CH_2{=}CH{-}C(Si(O\text{-}iso\text{-}C_3H_7)_3){=}CH_2$[1,2]. H. Ozaki, S. Nakahama *et al.* (1999, E866) investigated the polymerization of silicon-containing methacrylates such as $CH_2{=}C(CH_3){-}COO(CH_2)_3{-}Si(OCH_3)_3$, $CH_2{=}C(CH_3){-}COO(CH_2)_3{-}Si(OC_2H_5)_3$ and $CH_2{=}C(CH_3){-}COO(CH_2)_3{-}Si(O\text{-}iso\text{-}C_3H_7)_3$. Anionic polymerization of $CH_2{=}C(CH_3){-}COO(CH_2)_3{-}Si(OCH_3)_3$ and $CH_2{=}C(CH_3){-}COO(CH_2)_3{-}Si(OC_2H_5)_3$ with *n*-C_4H_9Li/1,1-diphenylethylene/LiCl system in tetrahydrofuran (THF) at −78°C for 1 hour yielded the polymers quantitatively. These monomers underwent anionic living polymerization. The gel permeation chromatographic measurements of the polymers obtained showed single peaks with very narrow molecular weight distributions. The polymers were found to be very sensitive to moisture and difficult to handle for further characterization. On the other hand, anionic polymerization of $CH_2{=}C(CH_3){-}COO(CH_2)_3{-}Si(O\text{-}iso\text{-}C_3H_7)_3$ produced stable polymer through a living polymerization mechanism mentioned above. Polymers possessing relatively broad molecular weight were obtained in the absence of LiCl.

The same research group (K. Takenaka, S. Nakahama *et al.*, 2002, E 867) reported more detailed study on anionic polymerization of silicon-containing butadienes such as $CH_2{=}CH{-}C(Si(OCH_3)_3){=}CH_2$, $CH_2{=}CH{-}C(Si(O\text{-}iso\text{-}C_3H_7)_3){=}CH_2$, $CH_2{=}CH{-}C(Si(CH_3)(O\text{-}iso\text{-}C_3H_7)_2){=}CH_2$, $CH_2{=}CH{-}C(Si(CH_3)_2(O\text{-}iso\text{-}C_3H_7)){=}CH_2$ and $CH_2{=}CH{-}C(Si(CH_3)_3){=}CH_2$ initiated with M^+ (α-methylstyrene)$_n^{2-}$ M^+ in THF at −78°C where M = Li, Na, K and Cs. The propagating species were found to be surprisingly stable in most cases since the brownish-orange color maintained more than 90 hours. The polymers derived from $CH_2{=}CH{-}C(Si(CH_3)(O\text{-}iso\text{-}C_3H_7)_2){=}CH_2$, $CH_2{=}CH{-}C(Si(CH_3)_2(O\text{-}iso\text{-}C_3H_7)){=}CH_2$ and $CH_2{=}CH{-}C(Si(CH_3)_3){=}CH_2$ were of controlled molecular weights and relatively narrow molecular weight distributions. The microstructures of the polymer obtained from $CH_2{=}CH{-}C(Si(OCH_3)_3){=}CH_2$ and $CH_2{=}CH{-}C(Si(O\text{-}iso\text{-}C_3H_7)_3){=}CH_2$ were predominantly 1,4-Z whereas 1,4-Z and 1,2-linkages were found to be contained in some extent in other poly(silyl-substituted butadienes). Block copolymerization initiated with living oligomers of $CH_2{=}CH{-}C(Si(O\text{-}iso\text{-}C_3H_7)_3){=}CH_2$, $CH_2{=}CH{-}C(Si(CH_3)(O\text{-}iso\text{-}C_3H_7)_2){=}CH_2$, $CH_2{=}CH{-}C(Si(CH_3)_2(O\text{-}iso\text{-}C_3H_7)){=}CH_2$, and $CH_2{=}CH{-}C(Si(CH_3)_3){=}CH_2$ by adding 2-vinylpyridine was found to be successful.

Y. Kawakami, T. Abe *et al.* (2059, E 887) prepared *ortho-*, *meta-* and *para-* isomers of trimethylsilyl-substituted and oligodimethylsiloxanyl-substituted styrene derivatives. The corresponding homopolymers of *meta-* and *para-*isomers were produced in reasonable yields under radical polymerization conditions though *ortho-*isomers failed to produce polymer. The existence of siloxane linkage as a spacer group between the polymer main chain and oligodimethylsiloxanyl group was essential to bring about the high gas permeability.

T. Higashimura and his coworkers discovered the polymerization of acetylene compounds with transition metal initiators.[3] K. Tsuchihara, T. Higashimura *et al.* (2056, E 886) applied the polymerization method to silicon-containing acetylene compounds such as $C_6H_5{-}C{\equiv}C{-}C_6H_4\text{-}p\text{-}Si(CH_3)_3$ and $C_6H_5{-}C{\equiv}C{-}C_6H_4\text{-}m\text{-}Si(CH_3)_3$. Polymerization of these two monomers catalyzed by $TaCl_5/(n\text{-}C_4H_9)_4Sn$ system gave the polymers in over 70% yields; although polymerization catalyzed by $TaCl_5$ itself produced only linear oligomers. The weight-average molecular weights of the polymers obtained were as high as 2×10^6. The polymers were soluble in various organic solvents such as toluene and chloroform, and tough films were obtained by solution casting. Weight loss started at 400°C or above, which showed appreciably high thermostability.

J. Oku and M. Takaki (2011, E 870) found the isomerization polymerization of trimethylvinylsilane, benzyldimethylvinylsilane and allyldimethylvinylsilane by the initiation of $sec\text{-}C_4H_9Li$ in the presence of N,N,N′,N′-tetramethylethylenediamine



$$CH_2{=}CH{-}Si(CH_3)_2(CH_2C_6H_5) \longrightarrow \left(CH_2{-}\underset{\substack{|\\ CH_2\\ |\\ Si(CH_3)_2(CH_2C_6H_5)}}{CH}{-}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{Si}}{-}\overset{\substack{C_6H_5\\ |}}{CH} \right)_n$$

(TMEDA).[4] The extent of isomerization was raised when the monomer concentration was low and/or the polymerization temperature was high in the case of trimethylvinylsilane to produce the polymers having silicon-carbon linkages in the main chain. The isomerization polymerization of benzyldimethylvinylsilane took place without TMEDA through abstraction of a benzylic proton one per two vinyl addition reactions.

H. Sakurai and his coworkers examined anionic polymerization of disilenes ($R_2Si{=}SiR_2$) to obtain polysilanes possessing silicon—silicon bond in main chain (K. Sakamoto, H. Sakurai *et al.*, 2017, E 872; M. Yoshida, H. Sakurai *et al.*, 2020, E 873; Y. Funada, H. Sakurai *et al.*, 2023, E 874).[5] Polysilanes are mostly prepared by Wurtz-type coupling reactions of dichlorodialkylsilanes with sodium, which have several difficulties such as poor control of structure, molecular weight and polydispersity. Instead of polymerization of disilene compounds which are unstable except for those with very bulky substituents, anionic polymerization of l-phenyl-7,8-disilabicyclo[2,2,2]octa-2,5-dienes as precursors of disilenes was investigated. The monomer was prepared from 1,2-dichloro-1,1,2,2-tetraalkylsilane with biphenyl anion radical. l-Phenyl-7,8-disilabicyclo[2,2,2]octa-2,5-diene produced the polymer with alkyllithium such as n-C_4H_9Li and sec-C_4H_9Li accompanied by the elimination of biphenyl. The polymer was identified as a polysilane structure $(-SiR_2-SiR_2-)_n$ in main chain by the measurements of ^1H, ^{13}C and ^{29}Si NMR. The molecular weight was about 5×10^4 and the molecular weight distribution ($\bar{M}w/\bar{M}n$) was around 1.5 which was narrower than that prepared by the conventional condensation method.

N. Kato, T. Tsuruta *et al.* (2005, E 868) reported the syntheses of novel organosilicon-containing oligomers and macromonomers. The reaction of 4-vinylbenzyllithium with 1,2-bis(chlorodimethylsilyl)ethane as difunctional counterpart produced oligomers possessing a molecular weight of 200–2000. UV, gel permeation chromatographic and ^1H NMR analyses showed that the oligomer was formed through anionic polycondensation of 4-vinylbenzyllithium with 1,2-bis(chlorodimethylsilyl)ethane without any side reactions, such as vinyl polymerization. The reaction of 4-vinylbenzyllithium with dichlorodimethylsilane as difunctional counterpart formed oligomers through anionic polycondensation.

The same research group also reported (Y. Nagasaki, T. Tsuruta *et al.*, 2008, E869) the syntheses of other macromonomers by the reaction of $CH_2{=}CH-Si(CH_3)_2-CH{=}CH_2$ or $CH_2{=}CH-Si(CH_3)_2-O-Si(CH_3)_2-CH{=}CH_2$ with N,N'-diethylethylenediamine in the presence of lithium diisopropylamide. The molecular weight of the macromonomers obtained was 1000–3000.

M. Suzuki, T. Saegusa *et al.* (2014, E 871) investigated the anionic ring-opening polymerization of 1,2-disilacyclopentane and 1,2-disilacyclohexane. 1,1,2,2-Tetramethyl-1,2-disilacyclopentane and l-phenyl-1,2,2-trimethyl-1,2-silacyclopentane were found to yield oligomers or polymers with CH_3OK, CH_3ONa and CH_3Li in the presence of hexamethyldisilane at 0°C. The addition of a polar aprotic solvent such as hexamethylphosphoric triamide and 1,3-dimethyl-2-imidazolidinone or a small amount of crown ether into THF was required. Living polymerization of l-phenyl-1,2,2-trimethyl-1,2-silacyclopentane took place by the initiation of $(C_6H_5(CH_3)_2Si)_2Cu(CN)Li_2$.

An invited lecture entitled "Polysilanes; Synthesis, Modification, and Properties" was presented by K. Matyjaszewski (E 875) of Carnegie Mellon University.

Fluorine-containing Polymers

A few papers have appeared concerned with research work on the preparation of new fluorine-containing polymers and on development of new polymerization reaction of fluorinated monomers from both academic and industrial research laboratories.

Y. Yamamoto and M. Tatemoto (1981, E 859) reported the copolymerization of tetrafluoroethylene (TFE) with α, ω-divinylperfluoroalkanes ($CH_2{=}CH{-}R_f{-}CH{=}CH_2$). The copolymers were prepared from combinations of TFE with 1,6-divinylperfluorohexane and TFE with 1,8-divinylperfluorooctane without radical initiators. The melting behavior of the copolymers obtained was found to be different from that of poly(tetrafluoroethylene) (PTFE); which suggested trace amounts of divinyl compound were incorporated in the polymer main chain although the copolymers were spectroscopically similar to PTFE and the divinyl compound unit was not detected by infrared spectrum. According to the electron spin resonance measurements, the concentration of active species of the propagating chain end was much lower than that of gamma-ray initiated radical polymerization of TFE by the order of 10^{-4}. The rate studies, on the other hand, revealed that the copolymerization rates of TFE with 1,6-divinylperfluorohexane was 60 times faster than that of gamma-ray initiated homopolymerization of TFE.

M. Tatemoto *et al.* developed "Iodine-transfer Polymerization" and this applied method to the preparation of block-copolymer of 1,1-bis(trifluoromethyl)ethylene with TFE in the presence of 2-iodoperfluoropropane as a chain transfer agent, to produce thermoplastic fluoroelastomers. The polymerization system showed the living polymerization characteristics.[6] M. Tatemoto (1984, E 860) reported a new curing method of the block-copolymer to improve oleophorbicity and brittleness at high temperature. The curing process was carried out with triallyl isocyanurate and 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3 as curing agents. The cross-linked elastomer showed very high tensile strength, up to 500 Kg/cm^2.

Anionic polymerization of hexafluoro-1,3-butadiene (HFBD), which is hardly polymerized under radical polymerization conditions, was reported by T. Narita, T. Hagiwara *et al.* (1987, E 861). Poly(HFBD) was easily prepared by the initiation of CsF, as reported previously.[7] More detailed study revealed that *tert*-C_4H_9OCs, $Cs^+(\alpha\text{-methylstyrene})_n^{2-}\ Cs^+$, cesium naphthalene, RbF, *tert*-C_4H_9ORb, $Rb^+\ (\alpha\text{-methylstyrene})_n^{2-}\ Rb^+$, and rubidium naphthalene were found to show surprisingly high activity. Anionic polymerization of HFBD initiated with *tert*-C_4H_9OCs, for example, produced 83.9% yield of poly(HFBD) in toluene at 60°C for 3 hours. The ionic radius of countercation might thus be important in this polymerization system. The initiation reaction of HFBD with *tert*-C_4H_9OCs in THF at 0°C and -78°C was examined by measurement of the concentration of *tert*-C_4H_9OCs. The reaction was found to be completed within 5 minutes although the reactions were carried out at much lower temperatures than those of polymerization reaction. The initiation reaction was, therefore, inferred to take place in an anionic fashion by adding *tert*-butoxide anion to HFBD. The microstructure of poly(HFBD) was estimated to be 1,4-addition sequence in main chain derived from ^{13}C NMR and infrared spectra. Higher thermostability of poly(HFBD) than PTFE was confirmed by the measurements of differential scanning calorimetric analysis. A more detailed study on the relationship between thermal properties and structures of poly(HFBD) was also reported (S. Nishimura, T. Narita *et al.*, 2119, E 907).

Anionic polymerization of fluorine-containing vinyl monomers was also reported by T. Ogawa, S. Inoue *et al.* (1990, E 862). The research group previously found that organoaluminium compounds complexed with tetraphenylporphyrin are excellent initiators for the living polymerization of alkyl methacrylates to afford polymers of controlled molecular weight with narrow molecular weight distribution (Immortal polymerization). Living polymerization of fluorine-containing methacrylates such as $CH_2{=}C(CH_3){-}COOCH_2CF_3$, $CH_2{=}C(CH_3){-}COOCH(CF_3)_2$ and $CH_2{=}C(CH_3){-}COOCH_2CH_2C_8F_{17}$ was investigated with aluminium porphyrin derivatives as initiators. Polymerization of $CH_2{=}C(CH_3){-}COOCH_2CF_3$ with methylaluminium tetramethylporphyrin produced 100% yield of the polymer within 220 minutes at 35°C under the irradiation of visible light. Molecular weight distribution of the polymer obtained was very narrow. Block copolymerization of methyl methacrylate or propylene oxide with living polymers prepared from fluorinated methacrylates was also reported to be successful.

Ring-opening polymerization of fluorinated epoxides hardly produces polyethers possesing high molecular weight.[8] Polymerization of hexafluoropropylene oxide yields oily oligomers which are applied as high performance lubricant and vacuum-pump oil. Anionic polymerization of 3,3,3-trifluoro-1,2-epoxypropane (TFEP) initiated with organozinc compounds and alkali metal *tert*-butoxides was investigated by T. Hagiwara, T. Narita *et al.* (1993, E 864). TFEP was found to produce polymers with organozinc initiators such as $Zn(C_2H_5)_2$, $(C_2H_5ZnOCH_3)_4$, $[Zn(OCH_3)_2(C_2H_5ZnOCH_3)_6]$ and $[Zn(OCH_3)]_n$, some of which are unable to polymerize propylene oxide. $[Zn(OCH_3)_2(C_2H_5ZnOCH_3)_6]$ showed excellent activity to give 100% yield in benzene and in 94% in 1,2-dimethoxyethane (DME) at 80°C. No solvents were found to dissolve the polymer obtained, except THF and DME but with difficulty. Molecular weight measured by gel permeation chromatography was 1.0×10^6. Polymerization initiated with *tert*-C_4H_9OK, *tert*-C_4H_9ORb, *tert*-C_4H_9OCs also produced poly(TFEP). The molecular weight of the polymer obtained with *tert*-C_4H_9OCs was 4.3×10^3. ^{13}C and ^1H NMR analyses of the polymers showed that simple ring-opening reaction took place at either $CH_2{-}O$ (more probable) or $CH{-}O$ bond in the case of organozinc initiators, while random copolymerization of the $CH_2{-}O$ scission and $CH{-}O$ scission species took place by the initiation of *tert*-butoxides.

Synthesis and properties of polyimides having a perfluorononenyloxy group were reported by M. Yusa, Y. Miyadera *et al.* (2089, E 897). 1,3-Diamino-5-(perfluorononenyloxy)benzene was synthesized from 5-(perfluorononenyloxy)isophthalic acid with a modified Curtius reaction. Polyimides were synthesized by the polycondensation of 1,3-diamino-5-(perfluorononenyloxy)benzene with 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride or 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride in dimethylacetamide under 5°C, followed by heating at 250–300°C. The dielectric constant of polyimide was found to decrease with increasing fluorine-content of the polymer. The glass transition temperature of polyimide having perfluorononenyl groups scarcely decreased. Initial weight loss temperature was recorded at 403–405°C.

An invited lecture entitled "Determination of the molecular weight distribution from dynamic measurements of polymer melts" was presented by W.H. Tumenello of E.I. du Pont Company (E 863).

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