

Young-Gu Cheun

Cationic Copolymerization of 2-Butyl-1,3-dioxepane and 1,3-Dioxolane

Korea Polymer Journal, 2(1), 1(1994)

Copolymerization of 2-butyl-1,3-dioxepane (2-Bu-DOP) with 1,3-dioxolane (DOL) was carried out with boron trifluoride etherate ($\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$) as an initiator and the mechanism was investigated theoretically using semiempirical modified intermediate neglect of differential overlap (MINDO/3), modified neglect of diatomic overlap (MNDO), and Austin Model 1 (AM_1) methods. The nucleophilicity and the reactivity of cyclic acetals were explained by the negative charge on the oxygen atom and the LUMO energy of propagating species of cyclic acetals. The GC determination of unreacted monomers during the copolymerization indicated that the preferential polymerization of 2-Bu-DOP had occurred. The values of reactivity ratios, calculated by the Fineman-Ross method, were $r_A = 2.13 \pm 0.05$ and $r_B = 0.12 \pm 0.05$ at -10°C . Relative equilibrium concentration of cyclic oxonium ions (1) and the open carbenium ion (2) is considered very important to determine the copolymerization mechanism. The reactivity of 2-Bu-DOP containing butyl substituent at 2-position can affect the relative computational stability of oxonium ion by 5~7 kcal/mol favoring the carbenium ion. Considering the rapid equilibrium of these two cations and the reaction coordinate based on calculations, the chain growth via SN_1 mechanism might be as fast as that via SN_2 mechanism.

Doo Whan Kang*, Nak Jin Chung, and Ji Hum Baek
Synthesis and Photocharacteristics of Photosensitive Functional Group Substituted Silicone Polymer

Korea Polymer Journal, 2(1), 8(1994)

Diazonaphthoquinone-5-sulfonyl polycarbosilane (DNP) was synthesized by reacting diazonaphthoquinone-5-sulfonylchloride with poly(aminopropyl carbosilane), prepared from polycarbosilane and allylamine. Cinnamoyl group substituted polysiloxane copolymer was prepared by reacting poly(dimethyl-co-methylaminopropylsiloxane) with cinnamoyl chloride. Photosensitivity and contrast of these polymers depended on the kinds and quantities of the sensitizers. In case of DNP, the sensitivity was 240~350 mJ/cm² and the contrast was 1.48~2.07. A theoretical equation for the change of the resist film thickness as a function of the exposure time was derived. From the theoretical equation, the profile of the film thickness change at various exposure times could be simu-

lated using the optical parameters calculated from the optical transmittance measurements of the exposed film. The sensitivity value determined from the equation was similar to the one obtained from the conventional yield of residual film method.

Ki Ho Lee and Dong Choo Lee*

Phase Equilibrium of the Ternary System Composed of Polystyrene/Poly(n-butyl methacrylate)/Cyclohexane

Korea Polymer Journal, 2(1), 16(1994)

The phase behavior of three component system composed of well fractionated polystyrene, poly(n-butyl methacrylate), and cyclohexane was investigated by means of turbidimetry and gel permeation chromatography. Variations of the polymer concentration and the temperature lead the ternary system to be separated into two phases. Cloud point curves were determined as the function of mixing ratio of the two polymers, molar mass, temperature, and concentration. Equilibrium phase diagrams and tie lines for a number of partially miscible systems were constructed for the temperature range of 10.9~26.7 $^\circ\text{C}$ under atmospheric pressure. The polymer-polymer interaction parameters calculated based on the Flory-Huggins theory by using the experimentally obtained phase composition data and the polymer-solvent interaction parameters of binary systems, were found to be in the range of -0.0761~0.1900. All the experimental results lead to a conclusion that the difference of the molar mass between the two polymers is the most important factor in enhancing the miscibility of the incompatible polymers.

Jungahn Kim*, Kwang Ung Kim, and Roderic P. Quirk

Synthesis of Poly(styrene-*b*-ethylene) and Its Chain-end Carboxylation via Anionic Polymerization

Korea Polymer Journal, 2(1), 23(1994)

The direct synthesis of poly(styrene- β -ethylene) and its chain-end carboxylation have been investigated by a combination of size exclusion chromatography (SEC) and ^1H NMR spectroscopic analysis. The block copolymer and the chain-end carboxylated block copolymer are obtained from the sequential ethylene monomer addition to poly(styryl)lithium at 50 $^\circ\text{C}$ in cyclohexane and the direct reaction on poly(styrene- β -ethenyl) lithium including TMEDA with CO_2 gas, respectively. The molecular weight of the polyethylene block is low due to the insolubi-

lity in hydrocarbon solvent.

Jae-Hee Jung, Yong-Kiel Sung, Chong-Su Cho, and Young-Moo Lee

Thermo-sensitive Interpenetrating Polymer Networks Composed of Poly(N-vinyl pyrrolidone-co-butyl methacrylate) and Poly(acrylic acid)

Korea Polymer Journal, 2(1), 27(1994)

The swelling behavior of interpenetrating polymer networks (IPNs) composed of poly(N-vinyl pyrrolidone-co-butyl methacrylate) [p(NVP-co-BMA)] and poly(acrylic acid) (PAAc) in water was studied and compared with crosslinked p(NVP-co-AAc-co-BMA). The IPNs were synthesized by a sequential IPN method in which crosslinked PAAc chains were formed inside of p(NVP-co-BMA) networks as initial gels. Positive swelling changes were observed with temperature changes for IPNs gels containing higher BMA content while negative swelling changes were observed for random gels. The positive temperature dependence is regarded as the formation and dissociation of hydrogen-bond complexes between NVP and AAc with temperature changes in IPNs gels. The difference in temperature dependence of swelling between IPNs and random gels was attributed to the structural differences of the polymers.

Jin Ho Lee*, Heoung Woo Kim, Pyong Ki Pak, Sung Soo Kim, and Hai Bang Lee

Protein Behavior on Polymer Surfaces with Hydrophilic Functional Groups

Korea Polymer Journal, 2(1), 32(1994)

Surfaces with hydrophilic functional groups were prepared on low density polyethylene (PE) sheets by corona discharge treatment, followed by graft copolymerization of acrylic acid (-COOH, negatively chargeable) or acryl amide (-CONH₂, neutral). The prepared surfaces were characterized by the measurement of water contact angle, electron spectroscopy for chemical analysis (ESCA) and Fourier-transform infrared spectroscopy in the attenuated total reflectance mode (FTIR-ATR). It was observed that the wettability of the functional group-grafted surfaces increased largely compared to control surface but was not much affected by the kind of grafted functional groups (-COOH and -CONH₂ groups). The adsorption and desorption behavior of blood proteins such as albumin, γ -globulin, and fibrinogen on the control (hydrophobic) and the functional group-grafted (hydrophilic) surfaces was investigated in this study. The control PE surface showed large adsorption and desorption of the proteins due to the hydrophobic character. For the functional group-grafted surfaces, the surface grafted with -COOH groups showed less protein adsorption than that

grafted with -CONH₂ groups probably due to the negatively chargeable character in aqueous protein solution. Among the proteins used, fibrinogen was adsorbed most largely on the surfaces. It may be due to its unusually long three-dimensional structure with high molecular weight.

Ki-Chang Lee* and Mitchell A. Winnik

Odd-Shaped "Sponge-like" Particles Prepared by Non-aqueous Dispersion Polymerization

Korea Polymer Journal, 2(1), 40(1994)

A method is described for the preparation of the core-shell latex particle containing a cross-linked core and a polar shell in submicron size range and of the odd shaped "sponge-like" aggregates in 3 to 5 μ m using non-aqueous dispersion (NAD) polymerization. These latexes were prepared by seeded semi-continuous dispersion polymerization in *n*-heptane, and sterically stabilized by the poly(12-hydroxy stearic acid) (PHS) type amphipatic stabilizer. The final shapes of the resulting core-shell dispersion particles were found to be greatly influenced by the detailed composition of the monomer mixtures in the reaction. The aggregates formed in this study were easily redispersed after settling under the influence of the gravity. The freeze-dried core-shell particles were easily redispersed in water containing an amine base.

Ki-Chang Lee* and Mitchell A. Winnik

Odd-Shaped "Raisin-like" Particles Prepared by Non-aqueous Dispersion Polymerization

Korea Polymer Journal, 2(1), 47(1994)

Non-aqueous dispersion particles containing a cross-linked core and a polar shell were prepared by 3 stage dispersion polymerization in the presence of unsaturated poly(isobutylene) as a steric stabilizer. When a cross-linker was present in second-stage polymerization, the second-stage particles, and the subsequent third-stage particles, had a shrunken, raisin-like appearance with a narrow size distribution. The formation of raisin-like particles might be related to the interpenetrating network (IPN) structure in the PMMA seeds and phase separation within the particles in the presence of a cross-linker. The freeze-dried core-shell particles were easily redispersed in water containing amine base.

Moon Soo Park

Synthesis of Crosslinked Poly(methyl methacrylate) Beads in Emulsifier-free Emulsion Polymerization

Korea Polymer Journal, 2(1), 54(1994)

Monodisperse poly(methyl methacrylate) beads were

prepared in a single stage emulsion polymerization in the absence of emulsifier. The size of poly(methyl methacrylate) beads was almost independent of the polymerization temperature between 60 °C and 90 °C. Difference in the molecular weight and molecular weight distribution between polystyrene and poly(methyl methacrylate) suggests that the reaction takes place via a different polymerization mechanism. In order to use poly(methyl methacrylate) beads as filler particles in polymer composites, they were copolymerized with a crosslinking agent, such as allyl methacrylate or ethylene glycol dimethacrylate. Bead size remained unchanged with the variation of crosslinking density, while glass transition temperature increased with increasing concentration of crosslinking agent. A higher glass transition temperature manifests that ethylene glycol dimethacrylate is a better crosslinking agent than allyl methacrylate. 5 mol % crosslinking resulted in a 20 °C increase in glass transition temperature.

Hyun-Kuk Choj*, Jaekyeung Park, and Takeshi Endo
Photo-induced Cationic Ring-opening Polymerization of 2-Alkenyl-4-methylene-1,3-dioxolanes by Benzylsulfonium Salt

Korea Polymer Journal, 2(1), 61(1994)

Preparation of 4-methylene-1,3-dioxolane derivative

(**Ia, Ib**) with benzyl-4-hydroxyphenyl methylsulfonium hexafluoro-antimonate (BSS) is described. Unsaturated cyclic acetals **Ia, Ib** were synthesized by dehydrochlorination of 4-chloromethyl-1,3-dioxolane derivatives, which were easily prepared from acrolein derivative and 3-chloro-1,2-propane diol with sodium methoxide at ambient temperature. The photo-induced cationic polymerization with BSS yielded soluble poly(keto-ether)s containing carbon-carbon double bond, whereas the cationic polymerization of **Ia, Ib** with $\text{CH}_3\text{SO}_3\text{H}$ at ambient temperature produced crosslinked polymers.

In-Joo Chin*, Dong Sung Kim, Dae Won Moon, and Kyung Joong Kim

Biased Referencing for the XPS Analysis of Polymers

Korea Polymer Journal, 2(1), 66(1994)

Biased referencing, which involves the combination of gold decoration and electron charge neutralization by an electron flood gun, was investigated for the XPS analysis of nonconducting polymers. Biased referencing provided calibration of sample core level ionizations to the Fermi level of Au 4f_{7/2} set at a conductive value of 84.0 eV. Reproducible high resolution spectra of various polymers were obtained and the measured binding energies were compared with the literature values.

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