



# Phase equilibria and the surface tension of polypropylene polyol series in water/methanol mixtures: A consideration of structural effects



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## ABSTRACT

The phase equilibria and surface tension of a polypropylene polyol (PPP) series was studied in aqueous solvent systems. The PPP series was composed of ethylene oxide (EO) and propylene oxide (PO) groups, exhibiting specific interactions with both water and alcohols. Binary and ternary liquid-liquid equilibria (LLE) of the PPP series were determined via thermo-optical analysis (TOA) methods, which represented closed-loop miscibility in water and Treybal Type 1 behavior in water and methanol (MeOH), respectively. The surface tension of the ternary PPP1/water/MeOH system was measured using a well-known plate method. The dendritic characteristics of the PPP series were reflected through modeling using lattice cluster theory (LCT) for complex structures of the polymer. The phase diagrams and surface tension of the PPP series were described from binary to ternary systems based on LCT incorporated with Guggenheim's treatment using predetermined parameters. The calculated results of both systems were in good agreement with the experimental data using the same interaction energy parameters.

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## 1. Introduction

Polyols (polyhydroxyl compounds) are liquid substances containing at least two isocyanate-reactive groups [1,2]. Most polyols fall under one of three categories: polyether polyols, polyester polyols, or polycarbonate polyols. One of the most commonly used polyether polyols is polypropylene oxide (PPO). Numerous studies have paid particular attention to poly (ethylene oxide) (PEO) and PPO, which are well-known polymers exhibiting closed-loop phase behavior in water. Copolymers of the two repeating units also exhibit closed-loop miscibility. Likewise, common polyether triols with propylene oxide (PO) and ethylene oxide (EO) repeating units can be considered as components in 3-arm dendritic poly (propylene oxide-co-ethylene oxide) (P(PO-co-EO)) systems. Based on the structure and composition of the repeating units, many applications such as electrophoresis [3], dye-sensitized cells [4], solid polymer electrolytes [5,6], and drug delivery [7] have been studied recently.

Basically, closed-loop or lower critical solution temperature

(LCST) type phase behavior of PEO and PPO has been actively studied in recent decades. With regard to molecular weight, the closed-loop type phase diagrams of aqueous PEO or poly (ethylene glycol) (PEG) solutions were determined by many groups [8–10] between the range of 2000 to 100,000 Da. Due to the temperature range of experiments, the phase separation of PPO or poly (propylene glycol) (PPG) has rarely been a point of focus [8,11–13]. Copolymer [14] and ternary mixtures [12] of aqueous PEO and PPO systems were investigated to track changes in the separation regions with the addition of similar components.

Due to the dendritic or star-shaped structure of polymers, their physical properties are evidently varied compared to linear polymers containing the same repeating units. Yokoyama et al. [15] compared the coexistence curves and critical condition of star-shaped poly (styrene)s (PSs) containing 6.3 and 11.1 arms with those of linear polymers in cyclohexane. Striolo et al. [16] reported the osmotic second virial coefficient and intrinsic viscosity of both linear and 8-arm star-shaped PSs in various organic solvents via experimental and molecular simulations. To study the MW and detailed star-shaped structural effects of PSs in methylcyclohexane, Alessi et al. [17] investigated cloud point curves, critical conditions, and the coexisting densities and

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viscosities for both linear and star polymers. The aqueous solution behavior of linear and 4-arm star-shaped poly (N-isopropylacrylamide)s (PNIPAs) was also characterized via dynamic light scattering (DLS) and nuclear magnetic resonance (NMR) techniques [18]. Recently, the double stimuli-response of linear and 3–8 arm star-shaped poly (N,N-diethylaminoethyl methacrylate) (PDEA) in aqueous solutions was studied by measuring cloud points with respect to pH, temperature, MW, and structure [19]. Industrially, petroleum based dendritic polyether polyols or diols composed of EO and PO repeating units are an essential raw material used in the synthesis of poly (urethane) (PU) foams [20–24]. The structure-dependent thermodynamic properties of these polyols were investigated through correlation with homopolymers and copolymers [24–27]. The substitution of petroleum oil based polyols with natural oil based polyols has recently attracted attention and concern [20–22].

Since classical Flory-Huggins theory [28–31], a variety of thermodynamicists and experimentalists have developed and utilized convenient lattice-based models [32–39]. Among them, lattice cluster theory (LCT) was developed by Freed et al. [40–47] to obtain an exact mathematical solution for the liquid-liquid equilibria (LLE) of polymer solutions. Though the complexity of calculations has been pointed out, some revised LCTs [36,48–54] were reported to be applied as engineering tools. Prausnitz et al. suggested a thermodynamic analysis tool using LCT with an integral equation and Monte-Carlo simulation [55]. In our previous work, the LLEs of hyperbranched [49,51] and dendrimer solutions [50] were systematically described and correlated with experimental and molecular simulation results. By considering the oriented interactions between the specific parts of a component, a modified double lattice (MDL) model was derived by introducing a secondary lattice expression [54].

In addition to the LLE, considerable effort has been devoted to the investigation of the surface and interfacial tension of polymer solutions. In the early stage, Guggenheim presented a simple treatment in that the surface phase is regarded as a separated phase between the bulk liquid and vapor phases [56]. Gaines [57,58] and Prigogine and co-workers [59] reported a remarkably simple theory for the surface tension of polymer solutions based on Guggenheim's treatment; detailed derivation and analysis were presented in the work of Defay and Prigogine [60]. Furthermore, Siow and Patterson [61] extensively investigated the surface tension of polymer solutions using Flory-Huggins theory. The application of these theories to membrane formation were presented by Tanny [62]. In an attempt to describe the surface tension of organic mixtures, Nath [63] used an activity coefficient model for the conventional framework. However, to the best of our knowledge, simultaneous surface tension modeling with LLE is scarce. Recently, the interfacial behavior between two separated phases was analyzed using density gradient theory (DGT) as developed by Cahn and Hilliard [64] with a lattice model [65,66] and equation of state [67–69], respectively.

In this work, the LLE and surface tension of PPP in water and methanol (MeOH) mixtures were thermodynamically analyzed with both experimental and mathematical modeling. The LLE of each dendritic polymer with various solvent compositions was investigated via thermo-optical analysis (TOA) methods using the detection of transmitted light. The PPP series, considered as dendritic PO and EO copolymers, exhibits closed-loop type LLE in aqueous solutions. By adding MeOH as a cosolvent, the ternary systems represented Treybal [70] Type 1 phase behavior at moderate temperatures under isothermal conditions. Surface tension measurements for the ternary PPP1 solution were performed using a well-known Wilhelmy plate method between a

homogeneous phase temperature range. Quantitative analysis was performed by employing LCT with multi-component consideration. Binary and ternary LLEs were successfully correlated using the same model parameters. The surface tension of ternary PPP1 solutions was calculated using LCT combined with Guggenheim's treatment. It should be noted that the used interaction parameters were predetermined from the corresponding LLE calculations.

## 2. Experimental

### 2.1. Materials

Polypropylene polyol 1 ( $M_w = 1,200$  and  $EO\ wt\% = 0$ ), polypropylene polyol 2 ( $M_w = 3,000$  and  $EO\ wt\% = 8$ ), and polypropylene polyol 3 ( $M_w = 5,000$  and  $EO\ wt\% = 15$ ) samples were received from Mitsui Chemical & SKC Polyurethanes Inc (MCNS). PPP1, PPP2, and PPP3 were homo, block, and random copolymers, respectively. Fig. 1 depicts chemical structure of PPP series. Estimated  $n$  values of each  $(PO)_n$  and  $(EO)_n$  are provided in Table 1, when we assume PPP has equal length of 3-arms regardless of arrangement in copolymers. Distilled deionized water and methanol (MeOH) were obtained from Sigma-Aldrich.

### 2.2. Thermo-optical analysis (TOA) method [10]

The cloud points of PPP1, 2, and 3 in mixed solvent systems (water and MeOH mixture) were obtained by TOA, which measures the intensity of transmitted light with varying the temperature from the 1-phase to 2-phase. Instrument and setup for the method are described in Fig. 2. The setup consists of a central processor (Mettler FP 90), a heating-cooling chamber with a photo-diode (Mettler FP 82), a microscope (OLYMPUS BX40), and a PC for storing data. A Pyrex and quartz tube (i.d. = 1 mm and o. d. = 3 mm) were used for sample tube in moderate (up to 473.15 K) and high (over 473.15 K) temperature condition, respectively. After preparing the desired concentration of water/MeOH solutions, PPP was dissolved by agitating for 12 h, only which needs sample under 2 mL. Sufficiently low scan rates (0.1 °C/min) were adopted to detect an abrupt reduction in intensity, which corresponded to the transition temperature. The process for cloud point determination can be seen in Fig. 3 using part of the raw data.

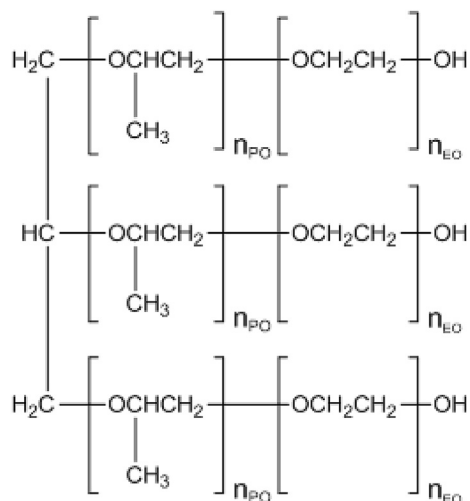


Fig. 1. Chemical structures of polypropylene polyol (PPP) series. The subscripts "PO" and "EO" represent "propylene oxide" and "ethylene oxide" repeating units.

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