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Cristina Mio, Simona Kiritsov, Yonathan Thio,  
Rebecca Brafman, John Prausnitz, Craig Hawker,  
and Eva E. Malmström

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# Vapor-Liquid Equilibria for Solutions of Dendritic Polymers

\*Cristina Mio, Simona Kiritsov, Yonathan Thio,

Rebecca Brafman and John Prausnitz \*

Department of Chemical Engineering

University of California

and

Chemical Sciences Division

Lawrence Berkeley National Laboratory

University of California

Berkeley, CA 94720, U.S.A.

and

Craig Hawker and Eva E. Malmström

Center for Polymeric Interfaces and Macromolecular Assemblies

IBM Almaden Research Center

650 Harry Road, San Jose, CA 95120-6099

April 1998

\*Istituto Impianti Chimici, Università di Padova, Italy

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## ABSTRACT

Vapor-liquid equilibrium data were obtained for dendritic polymer solutions using a classic isothermal gravimetric-sorption method; the amount of solvent absorbed by the dendrimer was measured at increasing solvent activity.

The polymers were polyamidoamine (PAMAM) dendrimers of generations 1, 2, and 4 and benzyl-ether dendrimers with different end groups (aromatic rings, dodecyl chains, methyl ester groups, perfluoroalkyl chains) of generations 2 to 6, and two series of benzyl-ether linear polymers that are analogs of the dendrimers.

Solvents were acetone, acetonitrile, chloroform, cyclohexane, methanol, n-pentane, n-propylamine, tetrahydrofuran and toluene. The temperature range was 35 to 89 °C.

The amount of solvent absorbed by the dendrimers depends, sometimes strongly, on the kind of dendrimer end groups. The relation between solvent absorption and dendrimer generation number, or molecular weight, depends on the solvent-dendrimer system and on temperature.

Solvent absorption in linear polymers is below that for corresponding dendrimers, all or in part, due to crystallinity in the linear polymers.

## INTRODUCTION

Dendrimers (also called cascade polymers or starburst molecules) are highly branched, tree-like macromolecules with a branch point at each monomer unit. They consist of a central core, concentric "shells" and an external surface. Each family of dendrimers, i. e. dendrimers made with the same repeat unit, consists of different generations, each corresponding to a different

number of shells around the core. In the past ten years many kinds of dendrimers have been synthesized. Detailed reviews are given by Tomalia and Durst (1993), Newkome (1994), Newkome et al. (1996), Frechet and Hawker (1996).

For dendrimers, the variety of molecular structure, size, shape, topology, flexibility and surface chemistry offers a wide variety of possible applications for these new materials. Organometallic dendrimers may provide a new class of advanced catalysts that combine the advantages of heterogeneous and homogeneous catalysis. Since the catalytic sites can be located at the surface of the dendrimer, the activity of each individual site is maximized. Recovery of the dendrimer catalyst is easily achieved by ultrafiltration due to the well-defined size of the macromolecules (Knapen, 1994).

Balzani (1994) suggests using transition metal-based dendrimers as devices for harvesting solar energy. The peripheral groups of the molecule collect sun light which is then channeled through the supramolecular dendrimer array and concentrated in a specific central site.

Potential dendrimer applications are also in medicine and biotechnology. For example, Wiener et al. (1994) studied the use of polyamidoamine (PAMAM) dendrimers as magnetic-resonance imaging contrast agents. Haensler and Szoka (1993) showed that PAMAM dendrimers are suitable for gene-transfer vehicles and Barth et al. (1994) studied the use of boronated dendrimers delivered by monoclonal antibodies in cancer therapy.

Dendrimers with an interior hydrophobic core surrounded by a hydrophilic surface layer behave as unimolecular micelles capable of solubilizing hydrophobic molecules in aqueous solutions without a critical micelle concentration (Hawker et al., 1993). These characteristics suggest application of dendrimers in a recyclable solubilization and extraction procedure that can be used in the recovery of organic substances from water. Jansen et al. (1994) demonstrated that it is

possible to encapsulate guest molecules in a dendritic polymer, the so-called “dendritic-box”, by constructing a dense shell in the presence of the guest molecules. In a successive paper (Jansen and Meijer, 1995) shape-selective liberation was studied for molecules trapped in the dendrimer. The capability of starburst molecules to host small molecules makes them attractive as drug-delivery agents (Tomalia, 1991). Further, if dendrimers are connected in a network, they could be used as filters, membranes, chromatographic materials and adsorbents. The ability to control their size, shape and surface chemistry offers ideas for applications as molecular electronic devices, biosensors, chemical sensors. For example, Wells and Crooks (1996) showed that dendrimer monolayers provide suitable interfaces for chemical sensing applications and that the film reactivity and selectivity toward vapor-phase dosants depend on the generation of PAMAM used. Grinthal (1993) affirms that polypropyleneamine dendrimers are easier to process than the analogous linear polymers, since they have lower viscosities. This property allows injection molding of some dendrimer thermoplastics even if the same is not possible for corresponding linear polymers.

The purpose of this work is to determine how polymer-solvent vapor-liquid equilibria (VLE) change with dendrimer generation number and with surface groups, and to what extent the solubility of a solvent in a dendrimer differs from that in a corresponding linear polymer of the same chemical structure.

This work reports binary VLE data for several polar and non-polar solvents in polyamidoamine (PAMAM) dendrimers (Generations 1, 2, 4), in benzyl-ether dendrimers with different end groups (Generations 2 to 6), and in linear benzyl-ether polymers.

## MATERIALS, EXPERIMENTAL METHOD AND RESULTS

Table 1 shows characteristics of the solvents. The solvents were degassed with a standard freeze-thaw procedure and used without further purification.

The PAMAM (polyamidoamine) dendrimers (G1, G2, G4, G=Generation) were bought from Dendritech through Aldrich (Milwaukee, WI, catalog numbers: 41,238-4, 41,240-6, 41,244-9 for G1, G2, G4 respectively). They had a 4-functional diamine core and primary amine ( $\text{NH}_2$ ) end groups. They are sequenced copolymers of ethylene diamine and methyl acrylate. The repeat unit is ( $\text{NCH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2$ ). Their properties are shown in Table 2. Their glass-transition temperatures are between 0 and 15 °C, increasing with generation number. Because PAMAM dendrimers are sold in methanol solution (20 % by weight of polymer), they must be dried before performing the VLE experiment. We used high vacuum (26.7-53.3 Pa) until the mass of the dendrimer solution was constant; we assumed then that no solvent was present. Due to strong hydrogen bonding between PAMAM and methanol, the removal of traces of methanol was slow; several days (from 5 to 7) were required to dry the dendrimers.

Keeping pure PAMAM dendrimers at 35-40 °C for several days should not affect their structure (Spindler, 1996). However, Dendritech warns that prolonged heating of dendrimer solutions at temperatures over 45 °C can lead to formation of defect structures; further, the presence of other components could affect stability. For our experimental apparatus, we could not use temperatures lower than 35 °C. Also, below about 50 °C, the vapor pressures of the solvents would be too low to perform a meaningful experiment.

Benzyl-ether dendrimers are synthesized with the convergent method: the construction of the macromolecule is started at what finally becomes its "periphery". 3,5-dihydroxyl benzyl alcohol

is the dendrimer building block (Hawker and Frechet, 1990). Because the core of the molecules is bifunctional, two main branches emanate from the interior.

We studied several types of benzyl-ether dendrimers, all with the same interior core but different end groups (aromatic rings (AR), dodecyl chains (C12), aromatic rings with a methyl ester group in para-position (ME), perfluoroalkyl chains ( $\text{CF}_3\text{-(CF}_2\text{)}_3\text{-CH}_2\text{-O-}$ ) (F)). Figure 1 shows the chemical structure of a dendrimer of generation 3. The dendrimers' characteristics are given in Table 3. D224 indicates an AR dendrimer formed by three generation-4 wedges linked to a central 3-functional core.

Benzyl-ether linear polymers were studied to compare the solvent absorption of polymers with the same chemical structure but different geometry.

There are two possible series of linear polymers analogous to the AR dendrimers (Hawker et al., 1997). The first, derived from the polymerization of 3-hydroxybenzylalcohol, can be considered the linear analog of the polyether dendrimer minus the numerous chain-end groups. The second, derived from 3-hydroxy-5-benzyloxibenzylalcohol, can be considered the "exact" linear analog of the dendrimers. With ELA-Gn we indicate the exact linear analog of the AR-Gn dendrimer. ELA and AR have exactly the same molecular formulae.

Table 4 gives characteristics of the linear and ELA polymers. L[7]2 is obtained by condensing two L[7] polymers, thus obtaining a linear polymer with two aromatic rings as chain ends.

The polydispersity of the benzyl-ether dendrimers and linear polymers is very low (1.002-1.01) due to the stepwise method used for their synthesis. The benzyl-ether dendrimers and linear polymers were synthesized at IBM Almaden Research Center, San Jose, CA.

Before starting the VLE experiment, the polymers were dried overnight under vacuum at 50-70 °C to remove any traces of solvents or monomers remaining after polymerization.

The experimental method for VLE of polymer solutions is based on the classical gravimetric sorption technique (see, for example, Panayiotou and Vera, 1984). The apparatus and experimental procedure are described in detail by Gupta and Prausnitz (1995).

Binary systems studied are given in Table 5. Experimental VLE are given in Table 6.

We plot the solvent liquid mass fraction ( $w_1$ ) versus solvent activity ( $a_1$ ), defined as the ratio of the pressure to the saturation pressure of the pure solvent ( $P/P^S$ ). We used the equations suggested by Daubert and Danner (1989) to calculate the saturation pressure.

The temperature was controlled within  $\pm 0.3$  °C. The uncertainty in the pressure reading is 0.13 kPa. The uncertainty in  $w_1$  is 5-10 % below  $w_1=0.1$  and 2-5 % above  $w_1=0.1$ .

### **SOLVENT-INDUCED CRYSTALLIZATION (SINC)**

Solvent-induced crystallization was observed during absorption of acetone at 50 °C; chloroform at 50 °C and toluene at 70 °C in AR-G3 (Figure 2); chloroform at 50 °C in ME-G2, G3, G4; toluene at 70 °C and acetone at 50 °C in ME-G4; THF at 70 °C in ELA-G4; chloroform at 50 °C in ELA-G3, G4; and toluene at 70 °C in ELA-G3, G4, G5.

The initial solvent-free polymer was in the amorphous state. At low solvent absorption, the polymer behaved in the usual way: absorption of the solvent in the liquid polymer increased with rising solvent vapor pressure; but when the solvent mass fraction had reached about 0.04, the polymer started to reject the solvent (Figure 2). This rejection corresponds to the onset of crystallization in the polymer; during this process, the solvent is rejected from the crystallizing regions that are not able to dissolve solvents, and the extent of absorption falls. At higher solvent pressure, the degree of crystallinity remains constant and further absorption of the solvent takes

place only in the non-crystalline regions.

Solvent-induced crystallization (SINC) phenomena have been reported previously, e. g. for polycarbonate films (Kambour et al., 1966), isotactic polystyrene (Overbergh et al., 1975), and isotactic polypropylene (Vittoria, 1991; Vittoria et al., 1989).

Crystallization of polymers is facilitated by absorption of organic vapor because the low-molecular-weight plasticizer significantly increases the rate of crystallization. The dissolved solvent increases the nucleation probability and facilitates a higher rate of chain-segment diffusion. Crystallization rates are maximum at the temperature where the effect of the thermodynamic driving force, which increases with subcooling,  $(t_m - t)$ , is balanced by the decrease in polymer mobility with cooling. The ability of the polymer to diffuse is proportional to  $(t - t_g)$ . Therefore, crystallization rates are maximum somewhere between melting temperature,  $t_m$  and glass-transition temperature,  $t_g$ .

The presence of a solvent lowers a polymer's  $t_g$  and  $t_m$ . When the amount of solvent in the polymer is sufficient to decrease  $t_g$  such that the polymer chains have enough mobility at  $t$ , and the degree of undercooling  $(t_m - t)$  is high enough, crystallization starts in the polymer. For AR-G3,  $t_g$  is near 40 °C and  $t_m$  is 125 °C. Absorption experiments were performed at 50 °C for acetone and chloroform and at 70 °C for toluene. At 70 °C, the amount of solvent required to induce crystallization was much less than that at 50 °C.

Following solvent-induced crystallization, crystallinity in the polymer samples was confirmed by a DSC (differential scanning calorimetry) experiment. For AR-G3,  $t_m$  was 125 °C. Generations 1 and 2 of these dendrimers are obtained as crystalline solids with  $t_m = 85$  and 110 °C respectively, while generations 3, 4 and 5 do not crystallize when synthesized (Hawker and Frechet, 1990).

For the ME-dendrimers, the higher the generation, the higher the amount of solvent required to crystallize the polymer. This trend follows because it is more difficult for larger molecules to arrange in an ordered way. Melting temperatures of the ME-dendrimers are 120, 122, and 94 °C for G2, G3, G4 respectively.

DSC was performed twice for each polymer sample that experienced SINC. The first DSC run was for the sample that had been used in the VLE experiment; that sample showed a clear peak indicating crystallinity in the polymer. After the first DSC run, the sample (now totally liquefied) was cooled to room temperature and the DSC run was repeated. The second thermogram did not show any crystalline peak. The polymer did not crystallize during the cooling process, whereas the sample from the VLE experiment did show crystallinity because plasticizing solvent had been present during the VLE experiment.

## DISCUSSION

PAMAM dendrimers are strongly hydrophilic polymers, completely miscible in water, lower alcohols, glycols and ethylenediamine. They are insoluble in non-polar solvents as confirmed by an experiment with carbon tetrachloride at 40 °C, when no absorption of the solvent was observed even at P/P<sup>S</sup> equal to 0.6. PAMAM dendrimers are stable in methanol at room temperature, but a side reaction, known as retro-Michael reaction, can occur. This reaction accelerates at higher temperature and in protic solvents. Although our experiments with methanol were not longer than one week, we cannot be certain that no reaction occurred. However, we were able to reproduce our data.

Low absorption was observed with n-propylamine, probably because this amine is not

sufficiently polar for the dendrimers. There is some adsorption of acetone in the PAMAM, but this may be caused by the Schiff base reaction: amines react strongly with molecules that contain an aldehyde or ketone group. The system PAMAM- chloroform at 35 °C shows a strange shape for the VLE curve: at the beginning the polymer does not absorb much chloroform, but above  $w_1=0.15$ , it appears that chloroform is a good solvent for these polymers. For all solvents studied here, the amount of solvent absorbed was higher for lower generations (Figure 3). This trend is the one we would expect from the molecular weight of the dendrimers: the lower the polymer molecular weight, the higher the miscibility of polymer and solvent.

For the AR and C12 dendrimers there is not much difference in solvent absorption for different generations. For the AR dendrimers, the aromatic-ring/oxygen ratio is constant for every generation. Therefore, no significant change in chemical composition of the dendrimer occurs when changing generation.

For the AR dendrimers, the data with acetone and chloroform at 50 °C show that G4 absorbs more than G5. However, at 70 °C, this trend is inverted: G5 or G6 absorb more chloroform, toluene (Figure 4) or THF (Figure 5) than G4. However, the difference in absorption is small and not significantly higher than the experimental uncertainty, as shown in Figure 4. We studied only generations lower than G6. Hawker et al. (1993), Naylor et al. (1989) and Hawker et al. (1997) reported that for dendritic macromolecules, the transition from an open to a more globular structure occurs near G4. Generations higher than 5 might show differences in thermodynamic behavior larger than those reported here.

As expected, the VLE behavior of dendrimers varies with the chemistry of the surface groups. Comparison between the amount of toluene absorbed by C12 and AR dendrimers shows that C12 dendrimers absorb more toluene than the AR dendrimers (Figure 4). This result is surprising

because the chemical affinity between the aromatic solvent and the dendrimer surface groups is expected to be stronger for the aromatic surface groups than for the paraffinic surface groups. Figure 4 shows that toluene is not a good solvent for AR dendrimers or, at least, not as good as suggested by the aromatic rings in the dendrimer. On the other hand, toluene and alkyl chains are compatible: toluene and octane mix well, and toluene is a good solvent for polyethylene above 60-70 °C (see Polymer Handbook, 1989). Therefore, a possible explanation for the fact that toluene is a better solvent for the C12 dendrimers than for the AR dendrimers is that the affinity between toluene and the aromatic rings of the dendrimer is decreased by oxygen atoms in the polymer.

Absorption of cyclohexane in the AR dendrimers (G4, G5, G6) at 60 °C is very small: at solvent activity 0.71 the solvent weight fraction in G4 is only 0.013. Therefore, it appears that the absorption of alkanes in the C12 dendrimers is due to the favorable presence of the C12 alkyl terminal groups, in spite of the unfavorable aromatic groups.

Acetone is a better solvent for AR than for C12 dendrimers, at least above  $w_1=0.05$ . Again, a likely explanation is that polar acetone interacts more favorably with the oxygen-containing groups of the AR dendrimers than with non-polar alkyl chains in the C12 dendrimers.

The magnitude of the change in polymer-solvent compatibility depends strongly on the chemistry of the end groups. D224 and F dendrimers show similar VLE behavior in acetone and toluene. Probably the surface groups (aromatic rings and perfluoroalkyl chains) are too similar with respect to these two solvents to show a significant difference in the VLE data.

The VLE data show that absorption and solubility properties of dendrimers can be altered dramatically by changing the dendrimer chain-end functional groups. The solution properties of dendrimers that are completely insoluble in some solvents (for example, AR dendrimers in

alkanes) or only partially compatible with other solvents (for example, AR dendrimers in toluene), are modified significantly by simply adding different end groups to the dendritic molecules (for example, the dodecyl chains of the C12 dendrimers).

We fitted our VLE data to Freed's lattice-cluster theory (LCT) (Freed and Bawendi, 1989; Nemirovsky et al., 1992) as applied by Lue and Prausnitz (1997) to dendritic polymers. LCT represent the properties of Flory's lattice much better than does Flory-Huggins theory; it fits polymer-solvent VLE data better (Mio et al., 1997). LCT theory has only one adjustable

parameter, interaction parameter:  $\chi = \frac{\epsilon z}{2kT}$ , where  $k$  is Boltzmann's constant,  $T$  is the temperature,  $z$ , the lattice coordination number (set equal to 6) and  $\epsilon$  is the energy parameter.

The other parameters used in LCT, called indices, are calculated from the geometry of the dendrimer molecules. Following Lue and Prausnitz (1997), who reported the indices for 3-functional-core dendrimers, it is straightforward to calculate the indices for our case, bifunctional-core dendrimers, given the generation number and the number of spacers per arm. Table 7 gives the geometric parameters of the dendrimer (spacer/dendrimer arm and total number of dendrimer segments,  $r$ ) together with the  $\chi$  parameter obtained from the fit. The negative values of  $\chi$  for the system C12 dendrimer in toluene cannot be due to highly favorable interactions (e. g. hydrogen-bonding). However, the negative  $\chi$  indicates that toluene is a very good solvent for C12 dendrimers.

Figure 6 shows that LCT gives a good fit for the C12 dendrimers, but LCT is not able to reproduce the VLE curve of the AR dendrimers with the same accuracy (Figure 7).

In general, the initial slopes of sorption curves for the AR dendrimers are larger than those for C12 dendrimers (Figure 4), especially at lower temperatures (50 °C). Larger slopes may be due to

the stiffness of the AR-dendrimers; further, at 50 °C, the polymers are only 10 °C above their glass-transition temperature. Therefore, the polymers cannot be easily permeated by the solvent. Only after some solvent has been absorbed does the polymer become sufficiently flexible and permeable. If a desorption experiment follows an absorption experiment, then, at the same solvent activity, the solvent mass fraction is higher for the desorption curve. Similar hysteresis phenomena have been observed previously (e. g. Bonner and Prausnitz, 1974); hysteresis is explained by the different bulk structure that the polymer assumes on desorption.

Because the linear polymers were in the semicrystalline state at the temperature of the experiment, or because they experienced SINC, it was not possible to compare data for liquid dendrimers and liquid linear polymers. Figures 5 and 8 show that, in general, linear polymers absorb less solvent than the corresponding dendrimers (L[7] data are discussed later). However, because linear polymers are semicrystalline while dendrimers are liquid with a lower  $t_g$ , solubility of a solvent in the linear polymers is lower. It was not possible to raise the experimental temperature above the  $t_m$  of the polymers due to limitations of the apparatus.

Because of crystallinity, it is not surprising that linear polymers absorb less solvent than dendrimers. Similarly, linear analogs are less soluble in solvents than dendrimers (Hawker et al., 1997).

The data presented in this work show that, at the same temperature, there is a significant difference in the absorption behavior of two chemically identical polymers, one dendritic (amorphous), the other linear (partially crystalline). This difference in solution properties follows from the branched structure of the dendrimer. Branching makes crystallization more difficult; therefore, the permeability of the highly branched polymer to the solvent exceeds that of the linear polymer.

In Figure 5 the sudden increase in THF absorption by ELA-G2 at 70 °C is caused by the dissolution of the polymer's crystalline regions by the solvent (Allen et al., 1965). At the beginning, the polymer is partially in the crystalline state, but at solvent activity around 0.6, enough solvent is present to dissolve all of the polymer, crystalline or amorphous, thus forming a liquid solution of polymer and solvent. Dissolution of the polymer's crystalline regions is also observed for L[7] with chloroform at 50 °C.

Since L[7] is the only sample with low enough  $T_m$  (70 °C), we can only compare VLE behavior of L[7] and AR-dendrimers at 70 °C or higher. At this temperature, there is no crystallinity. With toluene at 70 °C and chloroform at 70 °C, L[7] absorbs almost the same amount of solvent as AR dendrimers. L[7] absorbs more acetone than the dendrimers; with THF (Figure 5) this difference is larger (around 30% solvent weight fraction). Solvent molecules probably reach all segments of the L[7] molecules but not the internal groups of the dendrimers. This effect is more evident with THF and acetone probably because these solvents have a higher affinity with the ether links of the polymers. For toluene, there are two opposite effects: one is the steric hindrance, the other the different chemical affinity of toluene with the aromatic end-groups and the ether-linked internal groups. The segments of L[7] are more accessible to toluene than are the internal dendrimer groups, but toluene has higher affinity to the dendrimer-surface aromatic groups than to the ether-linked groups. While L[7] has only one aromatic chain-end, the dendrimer has several. Because these two effects work in opposite directions, the absorption of toluene in the dendrimer and in L[7] is roughly the same.

## CONCLUSIONS

VLE of solutions containing PAMAM dendrimers (G1, G2, G4), benzyl-ether dendrimers (from G2 to G6) or linear polymers were studied with several polar and non-polar solvents at 35-89 °C. The generation number does not significantly change the absorption behavior of dendrimers. Dendrimer surface-group chemistry is an important factor in determining the solubility of solvents in the dendrimers. The linear analogs absorbed less solvent than the dendrimers because they were partially in the crystalline state at the temperature of the experiment, while the dendrimers were liquid.

It is likely that there are larger differences in VLE of solutions containing linear or dendritic polymers occur for generation numbers higher than 5 for more dilute polymer solutions.

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## TABLES

Table 1. Properties of the solvents

Solvent	Supplier	Lot number	Purity
Acetone	Fisher Scientific, Pittsburgh, PA	952818	99.6%
Acetonitrile	Fisher Scientific, Pittsburgh, PA	932673	99.9%
Chloroform	Fisher Scientific, Pittsburgh, PA	952629	99.9%
Cyclohexane	Fisher Scientific, Pittsburgh, PA	952398	99.9%
Methanol	Fisher Scientific, Pittsburgh, PA	952430	99.9%
n-Pentane	Fisher Scientific, Pittsburgh, PA	920827	99+ %
n-Propylamine	Aldrich Chemical Company, Inc. Milwaukee, WI	24095-8	99+%
Tetrahydrofuran	Fisher Scientific, Pittsburgh, PA	902693	99.9%
Toluene	Fisher Scientific, Pittsburgh, PA	933715	99.9%

Table 2. PAMAM dendrimers' properties

Generation	Mw <sup>a</sup>	Surface Groups
1	1,430	8
2	3,256	16
4	14,215	64

<sup>a</sup> MW=molecular weight

Table 3. Properties of the benzyl-ether dendrimers

Polymer	Termination	Generation	MW	Surface Groups	$t_g^a / ^\circ\text{C}$
AR-G3	Aromatic ring	3	1,592	8	40
AR-G4	Aromatic ring	4	3,288	16	40
AR-G5	Aromatic ring	5	6,680	32	40
AR-G6	Aromatic ring	6	13,464	64	40
D224	Aromatic ring		10,116	48	40
F	Perfluoroalkyl chain	4	5,560	16	65
C12-G3	Dodecyl alkane	3	2,216	8	20
C12-G4	Dodecyl alkane	4	4,536	16	20
C12-G5	Dodecyl alkane	5	9,176	32	20
ME-G2	Methyl ester	2	976	4	29
ME-G3	Methyl ester	3	2,056	8	52
ME-G4	Methyl ester	4	4,216	16	59

<sup>a</sup>  $T_g$  = glass-transition temperature

Table 4. Properties of the benzyl-ether linear polymers

Polymer	MW	Total number of aromatic rings	Number of terminal aromatic rings	$t_m^a / ^\circ\text{C}$	$t_g / ^\circ\text{C}$
L[7]	850	8	1	70	2
L[15]	1,698	16	1	92	23
L[7]2	1,850	18	2	101	28
ELA G2	747	7	4	110	--
ELA G3	1,592	15	8	130	40-43
ELA G4	3,288	31	16	140	40-43
ELA G5	6,680	63	32	150	40-43

<sup>a</sup>  $T_m$  = melting temperature

Table 5. Systems studied

Polymer	Solvent	t / °C
AR-G3, AR-G4, AR-G5	Acetone	50
AR-G3, AR-G4, AR-G5	Chloroform	50
AR-G3, AR-G4, AR-G5, AR-G6	Toluene	70
C12-G3, C12-G4, C12-G5	Acetone	50
C12-G3, C12-G4, C12-G5	Chloroform	50
C12-G3, C12-G4, C12-G5	Cyclohexane	60
C12-G3, C12-G4, C12-G5	n-Pentane	40
C12-G3, C12-G4, C12-G5	Toluene	70
ME-G2, ME-G3, ME-G4	Chloroform	50
ME-G4, F, D224	Acetone	50
ME-G4, F, D224	Toluene	70
AR-G4, L[7]	Acetone	70
L[7], L[15], L[7]2	Chloroform	50
AR-G4, AR-G5, L[7]	Chloroform	70
AR-G4, AR-G6, L[7]	Toluene	70
AR-G4, AR-G6, L[7]	Tetrahydrofuran	70
AR-G4, L[15], L[7]2	Toluene	89
AR-G5, ELA-G5, L[15]	Tetrahydrofuran	70
ELA-G2, ELA-G3, ELA-G4	Chloroform	50
ELA-G2, ELA-G4	Tetrahydrofuran	70
ELA-G3, ELA-G4, ELA-G5	Toluene	70
PAMAM-G1, G2, G4	Acetone	35
PAMAM-G1, G2, G4	Acetonitrile	40
PAMAM-G1, G2, G4	Chloroform	35
PAMAM-G1, G2, G4	Methanol	35
PAMAM-G1, G2, G4	n-Propylamine	35

Table 6. Experimental Vapor-Liquid Equilibria

$w_1$  (POLY) = solvent weight fraction in the liquid phase in solution with the polymer "POLY"

P (kPa)=vapor pressure in kPa

ARGn= aromatic-ring-terminated benzyl-ether dendrimers of generation Gn

C12Gn=dodecyl-terminated benzyl-ether dendrimers of generation Gn

MEGn= methyl-ester terminated benzyl-ether dendrimers of Generation n

FGn= perfluoroalkyl-chain terminated benzyl-ether dendrimers of Generation F

L[n]= benzyl-ether linear polymer n

ELAGn= exact linear analog of the ARGn

Solvent: Acetone;  $t=50$  °C;  $P^S= 81.9$  kPa

$w_1$ (ARG3)	$w_1$ (ARG4)	$w_1$ (ARG5)	P / kPa
0.013	0.009	0.011	15.9
0.022	0.015	0.012	21.8
0.029	0.020	0.019	27.2
0.039	0.039	0.040	34.6
0.031	--	--	40.6
0.023	0.100	0.089	47.2
0.031	0.124	0.114	53.1
0.045	0.176	0.159	60.7
0.072	0.220	0.205	67.6
0.093	0.255	0.238	71.4

Solvent: Chloroform;  $t=50\text{ }^{\circ}\text{C}$ ;  $P^S=69.2\text{ kPa}$

$w_1$ (ARG3)	$w_1$ (ARG4)	$w_1$ (ARG5)	P / kPa
0.024	0.038	0.038	9.1
0.051	0.057	0.046	15.0
0.029	0.109	0.086	21.6
0.030	0.159	0.121	28.1
0.040	0.205	0.172	33.1
0.056	0.265	0.243	38.8
0.073	0.328	0.299	44.0
0.090	0.383	0.356	49.0
0.117	0.455	0.411	53.7
0.234	0.540	0.484	58.5

Solvent: Toluene;  $t=70\text{ }^{\circ}\text{C}$ ;  $P^S=30.1\text{ kPa}$

$w_1$ (ARG3)	P / kPa
0.020	5.4
0.018	8.7
0.011	9.8
0.014	10.4
0.012	11.1
0.014	15.5
0.019	20.1
0.030	24.3

Solvent: Toluene;  $t=70\text{ }^{\circ}\text{C}$ ;  $P^S=30.1\text{ kPa}$

$w_1$ (ARG4)	$w_1$ (ARG5)	$w_1$ (ARG6)	P / kPa
0.012	0.006	0.012	4.7
0.026	0.021	0.028	8.0
0.051	0.042	0.058	11.1
0.076	0.070	0.090	14.4
0.113	--	0.133	17.5
0.158	0.170	0.195	21.3
0.209	0.236	0.266	24.3

Solvent: Acetone;  $t=50\text{ }^{\circ}\text{C}$ ;  $P^S=81.9\text{ kPa}$

$w_1$ (D224)	$w_1$ (MEG4)	$w_1$ (FG4)	P / kPa
0.010	0.021	0.026	16.3
0.020	0.030	0.036	23.1
0.038	0.033	0.046	28.7
0.062	0.058	0.071	37.4
0.089	0.089	0.094	45.7
0.114	0.110	0.119	52.8
0.138	0.126	0.144	58.3
0.193	0.170	0.242	68.7

Solvent: Toluene;  $t=70\text{ }^{\circ}\text{C}$ ;  $P^S=30.1\text{ kPa}$

$w_1$ (D224)	$w_1$ (MEG4)	$w_1$ (FG4)	P / kPa
0.018	0.023	0.019	7.1
0.027	0.023	0.020	8.8
0.043	0.022	0.036	12.0
0.060	0.034	0.054	14.8
0.088	0.045	0.082	17.5
0.118	0.099	0.107	19.8
0.140	0.130	0.129	21.3

Solvent: Acetone;  $t=50\text{ }^{\circ}\text{C}$ ;  $P^S=81.9\text{ kPa}$

$w_1$ (C12G3)	$w_1$ (C12G4)	$w_1$ (C12G5)	P / kPa
0.011	0.014	0.011	13.3
0.025	0.026	0.022	22.1
0.035	0.034	0.029	30.0
0.053	0.050	0.043	38.2
0.070	0.067	0.056	45.9
0.094	0.087	0.073	53.3
0.124	0.116	0.095	61.7
0.159	0.148	0.120	68.9
0.200	0.185	0.147	74.3

Solvent: Chloroform;  $t=50\text{ }^{\circ}\text{C}$ ;  $P^S=69.2\text{ kPa}$

$w_1$ (C12G3)	$w_1$ (C12G4)	$w_1$ (C12G5)	P / kPa
0.083	0.080	0.079	11.5
0.130	0.124	0.122	18.1
0.182	0.178	0.179	24.8
0.270	0.265	0.269	34.6
0.358	0.360	0.364	42.9
0.458	0.466	0.476	52.7
0.600	0.622	0.645	60.7
0.653	0.690	0.718	62.7

Solvent: Cyclohexane;  $t=60\text{ }^{\circ}\text{C}$ ;  $P^S=52.0\text{ kPa}$

$w_1$ (C12G3)	$w_1$ (C12G4)	$w_1$ (C12G5)	P / kPa
0.034	0.033	0.030	9.5
0.069	0.067	0.058	15.9
0.099	0.098	0.089	21.1
0.154	0.153	0.136	28.5
0.211	0.211	0.184	35.3
0.294	0.296	0.261	42.1
0.367	0.371	0.313	45.4

Solvent: n-Pentane;  $t=40\text{ }^{\circ}\text{C}$ ;  $P^S=116.3\text{ kPa}$

$w_1$ (C12G3)	$w_1$ (C12G4)	$w_1$ (C12G5)	P / kPa
0.025	0.021	0.024	21.2
0.033	0.032	0.034	31.6
0.054	0.055	0.059	43.5
0.071	0.074	0.075	54.3
0.082	0.077	0.084	58.2
0.106	0.104	0.110	70.9
0.156	0.156	0.169	86.4
0.221	0.225	0.250	100.6

Solvent: Toluene;  $t=70\text{ }^{\circ}\text{C}$ ;  $P^S=30.1\text{ kPa}$

$w_1$ (C12G3)	$w_1$ (C12G4)	$w_1$ (C12G5)	P / kPa
0.064	0.053	0.058	5.2
0.106	0.090	0.093	8.5
0.157	0.129	0.138	11.7
0.205	0.169	0.178	14.3
0.262	0.218	0.226	17.0
0.323	0.262	0.278	19.9
0.435	0.338	0.365	23.3

Solvent: Chloroform;  $t=50\text{ }^{\circ}\text{C}$ ;  $P^S=69.2\text{ kPa}$

$w_1$ (MEG2)	$w_1$ (MEG3)	$w_1$ (MEG4)	P / kPa
0.018	0.022	0.054	9.3
0.033	0.039	0.082	15.7
0.045	0.035	0.089	22.1
0.051	0.044	0.118	28.3
0.084	0.065	0.203	34.3
0.100	0.084	0.260	39.3
0.121	0.091	0.302	43.9
0.177	0.116	0.346	49.6
0.271	0.159	0.403	54.8

Solvent: Acetone;  $t=70\text{ }^{\circ}\text{C}$ ;  $P^S=159.5\text{ kPa}$

$w_1$ (L[7])	$w_1$ (ARG4)	P / kPa
0.018	0.011	22.9
--	0.015	29.1
0.030	0.022	35.2
0.047	0.030	49.4
0.074	0.054	65.5
0.096	0.071	78.5
0.128	0.097	95.3
0.162	0.121	109.1
0.181	0.131	113.5
0.187	0.139	118.1

Solvent: Chloroform;  $t=50\text{ }^{\circ}\text{C}$ ;  $P^S= 69.2\text{ kPa}$

$w_1$ (L[7])	$w_1$ (L[15])	$w_1$ (L[7]2)	P / kPa
0.007	0.003	0.004	7.9
0.026	0.021	0.007	16.4
0.036	0.032	0.012	23.8
0.052	0.048	0.019	31.3
0.168	0.082	0.030	39.3
0.185	0.094	0.037	41.3
0.314	0.122	0.048	48.6
0.355	0.140	0.064	51.9
0.412	0.166	0.087	57.0
0.463	0.189	0.161	61.5

Solvent: Chloroform;  $t=70\text{ }^{\circ}\text{C}$ ;  $P^S= 134.0\text{ kPa}$

$w_1$ (L[7])	$w_1$ (ARG4)	$w_1$ (ARG5)	P / kPa
0.012	0.008	0.016	7.1
0.024	0.022	0.034	17.4
0.051	0.043	0.056	23.7
0.082	0.072	0.092	34.7
0.123	0.107	0.132	46.5
0.166	0.152	0.176	57.9
0.207	0.190	0.215	68.9
0.258	0.230	0.262	78.9
--	0.287	0.320	90.6
--	0.353	0.389	102.7
--	0.441	0.486	113.3

Solvent: Toluene;  $t=70\text{ }^{\circ}\text{C}$ ;  $P^S= 30.1\text{ kPa}$

$w_1$ (L[7])	$w_1$ (ARG4)	$w_1$ (ARG5)	P / kPa
0.038	0.032	0.032	6.3
0.091	0.082	0.087	13.3
0.119	0.110	0.111	15.7
0.151	0.134	0.145	18.7
0.211	0.192	0.205	22.1
0.245	0.226	0.242	23.1

Solvent: Tetrahydrofuran;  $t=70\text{ }^{\circ}\text{C}$ ;  $P^S=115.2\text{ kPa}$

$w_1$ (ARG4)	$w_1$ (ARG6)	$w_1$ (L[7])	P / kPa
0.047	0.035	0.071	23.3
0.071	0.063	0.102	34.1
0.098	0.092	0.137	44.1
0.119	0.120	0.172	52.5
0.150	0.148	0.213	62.1
0.184	0.188	0.262	72.4
0.209	0.217	0.297	78.9
0.252	0.267	0.375	87.7
0.300	0.322	0.452	93.3

Solvent: Toluene;  $t=89\text{ }^{\circ}\text{C}$ ;  $P^S=60.1\text{ kPa}$

$w_1$ (L[15])	$w_1$ (L[7]2)	$w_1$ (ARG4)	P / kPa
0.010	0.005	0.029	7.9
0.022	0.023	0.053	15.7
0.026	0.029	0.058	21.5
0.033	0.043	0.102	28.8
0.046	0.069	0.138	36.7
0.053	0.081	0.166	43.1
0.058	0.081	0.176	44.5

Solvent: Tetrahydrofuran;  $t=70\text{ }^{\circ}\text{C}$ ;  $P^S=115.2\text{ kPa}$

$w_1$ (ARG5)	$w_1$ (ELAG5)	$w_1$ (L[15])	P / kPa
--	0.013	0.012	13.7
0.042	0.019	0.032	23.2
0.066	0.036	0.045	35.3
0.103	0.046	0.053	49.5
0.133	0.071	0.079	60.3
0.165	0.085	0.090	68.3
0.196	0.099	0.098	78.3
0.285	0.154	0.147	98.4

Solvent: Chloroform;  $t=50\text{ }^{\circ}\text{C}$ ;  $P^S=69.2\text{ kPa}$

$w_1$ (ELAG2)	$w_1$ (ELAG3)	$w_1$ (ELAG4)	P / kPa
0.010	0.008	0.025	11.5
0.014	0.076	0.089	27.9
0.015	0.101	0.136	34.3
0.027	0.135	0.171	42.5
0.028	0.177	0.206	49.5
0.036	0.204	0.237	56.3

Solvent: Tetrahydrofuran;  $t=70\text{ }^{\circ}\text{C}$ ;  $P^S=115.2\text{ kPa}$

$w_1$ (ELAG2)	P / kPa
0.006	22.7
0.012	65.9
0.284	78.7
0.306	82.9
0.334	87.0

Solvent: Tetrahydrofuran;  $t=70\text{ }^{\circ}\text{C}$ ;  $P^S=115.2\text{ kPa}$

$w_1$ (ELAG4)	P / kPa
0.012	13.1
0.027	23.1
0.032	34.8
0.055	48.1
0.068	60.7
0.089	72.1
0.129	92.3

Solvent: Toluene;  $t=70\text{ }^{\circ}\text{C}$ ;  $P^S= 30.1\text{ kPa}$

$w_1$ (ELAG3)	$w_1$ (ELAG4)	$w_1$ (ELAG5)	P / kPa
0.019	--	0.010	6.5
0.039	0.041	0.020	11.5
0.052	0.053	0.040	15.8
0.073	0.068	0.052	19.9
0.095	0.092	0.078	24.0

Solvent: Acetone;  $t=35\text{ }^{\circ}\text{C}$ ;  $P^S= 46.4\text{ kPa}$

$w_1$ (PAMAMG1)	$w_1$ (PAMAMG2)	$w_1$ (PAMAMG4)	P / kPa
0.010	0.012	0.001	9.5
0.013	0.013	0.008	12.0
0.014	0.017	0.012	16.3
0.025	0.021	0.019	22.1
0.056	0.047	0.048	27.5
0.141	0.124	0.113	30.0

Solvent: Acetonitrile;  $t=40\text{ }^{\circ}\text{C}$ ;  $P^S= 23.5\text{ kPa}$

$w_1$ (PAMAMG1)	$w_1$ (PAMAMG2)	$w_1$ (PAMAMG4)	P / kPa
0.012	0.011	0.007	12.5
0.024	0.021	0.019	16.8
0.046	0.046	0.037	20.1

Solvent: Chloroform;  $t=35\text{ }^{\circ}\text{C}$ ;  $P^S=39.9\text{ kPa}$

$w_1$ (PAMAMG1)	$w_1$ (PAMAMG2)	$w_1$ (PAMAMG4)	P / kPa
0.002	0.001	---	8.5
0.011	0.007	0.002	12.2
0.018	0.015	0.005	15.7
0.194	0.163	0.124	22.3
0.246	0.191	0.158	23.2
0.279	0.223	0.189	26.2
0.316	0.254	0.221	29.5
0.361	0.298	0.273	32.4
0.411	0.354	0.322	34.9

Solvent: Methanol;  $t=35\text{ }^{\circ}\text{C}$ ;  $P^S=27.9\text{ kPa}$

$w_1$ (PAMAMG1)	$w_1$ (PAMAMG2)	$w_1$ (PAMAMG4)	P / kPa
0.048	0.037	0.029	6.7
0.104	0.088	0.081	11.7
0.161	0.141	0.128	15.9
0.236	0.223	0.190	19.2
0.297	0.282	0.240	21.8
0.378	0.375	0.328	23.9

Solvent: n-Propylamine;  $t=35\text{ }^{\circ}\text{C}$ ;  $P^S=62.7\text{ kPa}$

$w_1$ (PAMAMG1)	$w_1$ (PAMAMG2)	$w_1$ (PAMAMG4)	P / kPa
0.004	0.003	0.002	18.1
0.007	0.008	0.004	24.2
0.014	0.017	0.007	29.7
0.025	0.026	0.019	34.8
0.041	0.041	0.035	40.2
0.071	0.071	0.065	47.2

Table 7. Parameters used with Lattice-Cluster Theory (LCT)

System	spacers/ arm	r (number of polymer segments)	$\chi$ (interaction parameter)
AR-G4 in Chloroform 50 °C	1	31	0.353
AR-G5 in Chloroform 50 °C	1	127	0.476
AR-G4 in Toluene 70 °C	1	31	0.875
AR-G6 in Toluene 70 °C	1	127	0.692
C12-G4 in Acetone 50 °C	2	61	1.144
C12-G5 in Acetone 50 °C	2	125	1.280
C12-G3 in Toluene 70 °C	1	15	-0.229
C12-G4 in Toluene 70 °C	1	31	-0.013
C12-G5 in Toluene 70 °C	1	63	-0.139

## Figure Captions

Figure 1. Chemical structure of a benzyl-ether dendrimer of generation 3. “EG” stands for “end group”. On the left, four different end groups are shown: aromatic rings, aromatic rings with a methyl ester group in para-position, dodecyl chains, perfluoroalkyl chains.

Figure 2. Activity of chloroform at 50 °C, acetone at 50 °C and toluene at 70 °C in AR-G3.  
Solvent-induced crystallization phenomenon

Figure 3. Activity of methanol at 35 °C in PAMAM-G1, G2, G4

Figure 4. Activity of toluene at 70 °C in AR-G4, AR-G5, AR-G6, C12-G3, C12-G4, C12-G5

Figure 5. Activity of THF at 70 °C in AR-G4, AR-G6, L[7], ELA-G2, ELA-G4

Figure 6. Fit (solid lines) with LCT of VLE data for C12-dendrimers in toluene at 70 °C (open symbols) and in acetone at 50 °C (solid symbols)

Figure 7. Fit (solid lines) with LCT of VLE data for AR-dendrimers in toluene at 70 °C (open symbols) and in chloroform at 50 °C (solid symbols)

Figure 8. Activity of toluene at 70 °C in AR-G4, AR-G5, AR-G6, ELA-G3, ELA-G4, ELA-G5

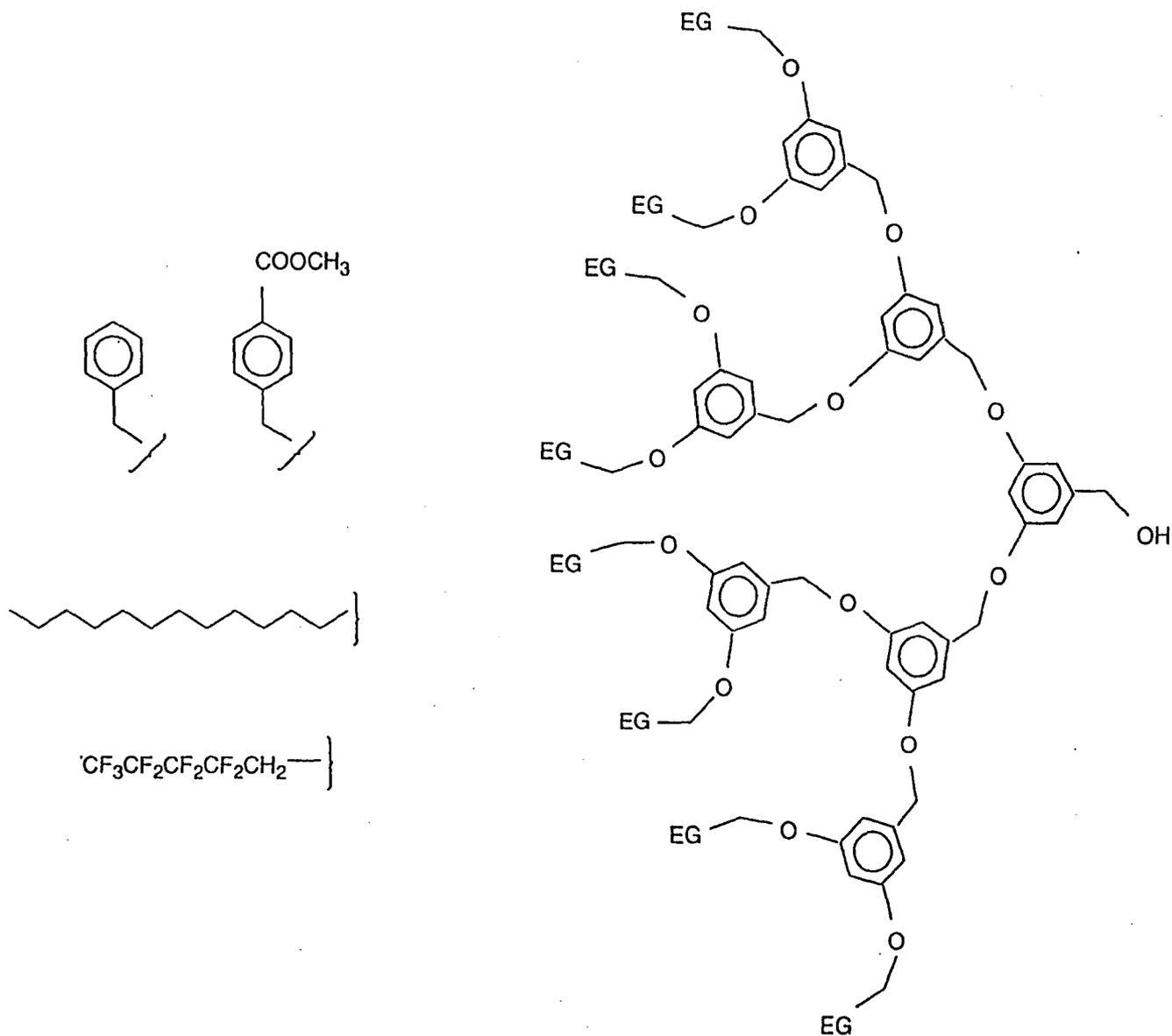


Figure 1

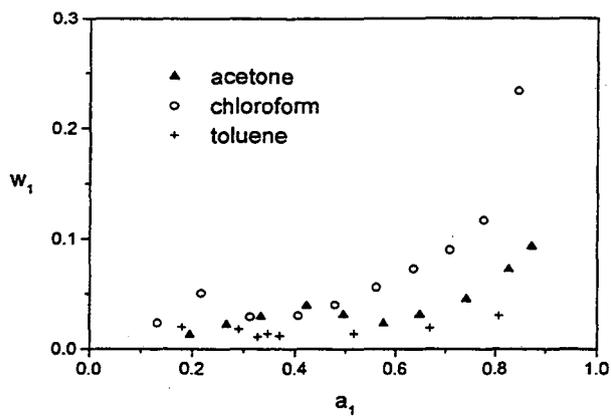


Figure 2

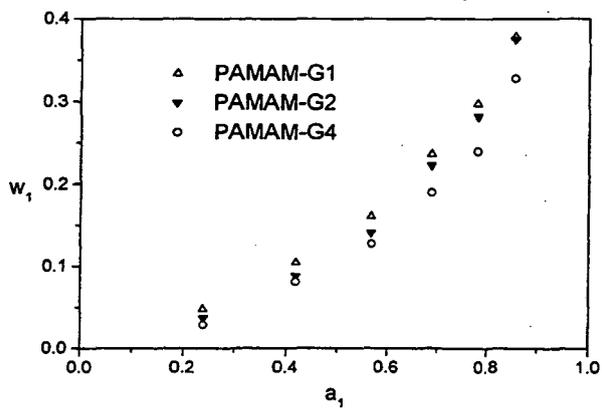


Figure 3

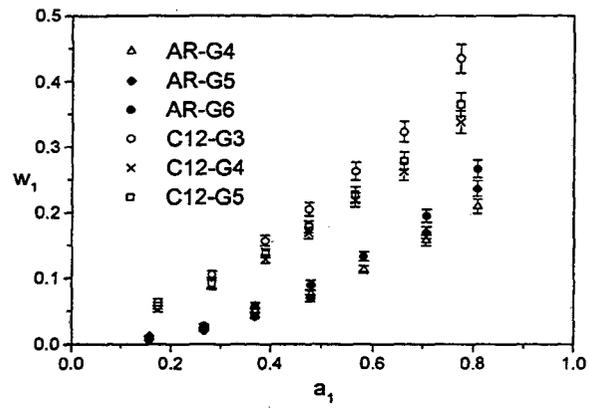


Figure 4

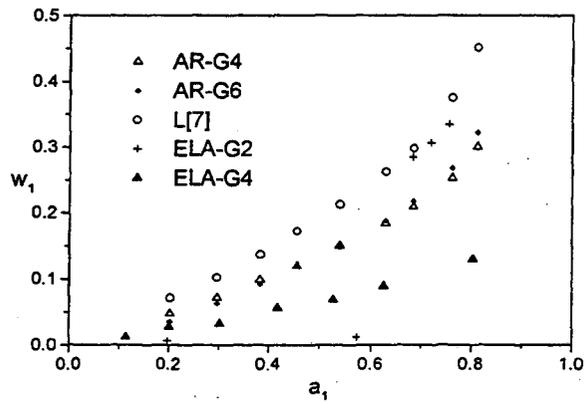


Figure 5

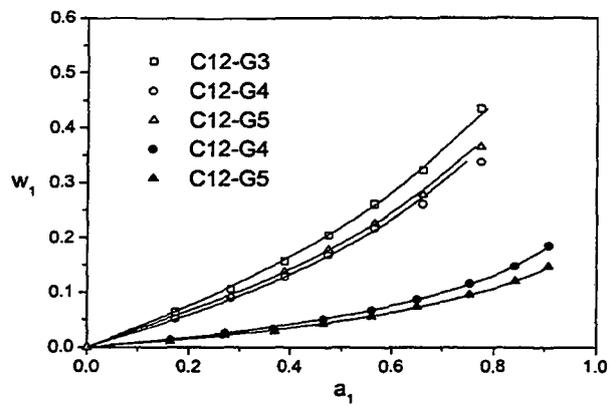


Figure 6

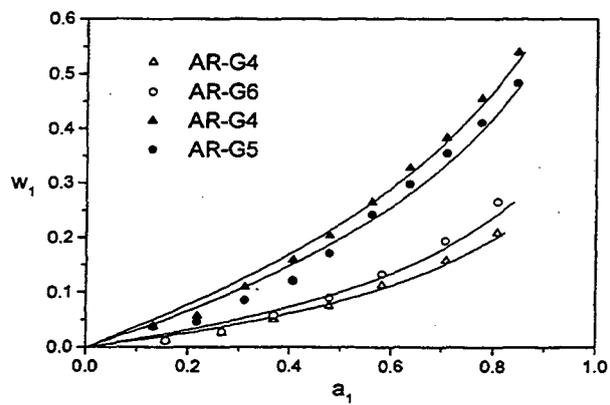


Figure 7

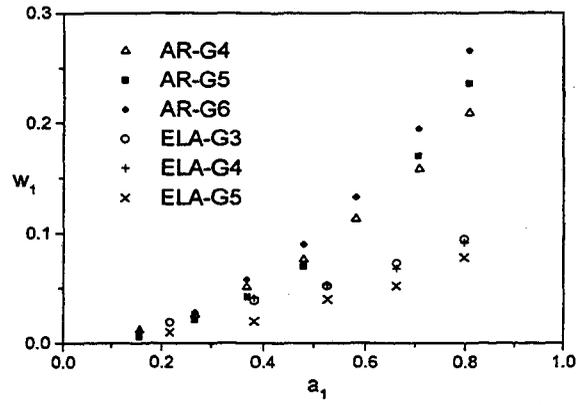


Figure 8

**ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY  
ONE CYCLOTRON ROAD | BERKELEY, CALIFORNIA 94720**