Solvent-Assisted Anionic Ring Opening Polymerization of Glycidol: Toward Medium and High Molecular Weight Hyperbranched Polyglycerols

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ABSTRACT: Hyperbranched polyglycerols (HPGs) are globular structures with a large number of functionalizable hydroxyl groups and have excellent *in vitro* and *in vivo* biocompatibility profiles comparable to polyethylene glycol. This work introduces a facile method for the synthesis of medium molecular weights (M_ws) (50–300 kDa) HPGs, which has been difficult to synthesize with low polydispersity, with the assistance of solvents by ring opening polymerization. The influence of different solvents (1,4-dioxane, tetrahydropyran (THP), ethylene glycol diethyl ether (EGDE) and decane), solvent to glycidol ratio, concentration of glycidol and the time of polymerization on M_w and polydispersity of HPGs has been studied. The M_w and polydispersity of HPGs are significantly affected by the nature of the polymerization phase (homogeneous or heterogeneous) and chemical structure of the solvent. The differences in the solvation of the potassium cations and change in the nucleophilicity of the alkoxide anion in various solvents may be responsible for the changes in M_w and PDI of the HPG. The M_w of the HPG decreases in the order 1,4-dioxane > THP > EGDE >decane. The microstructure, solution and thermal properties of the HPG do not depend on the nature of solvent. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 2614–2621

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INTRODUCTION Hyperbranched polyglycerols (HPGs) are globular biocompatible polymeric structures that contain a large number of derivatizable hydroxyl groups.[1–5] The number of hydroxyl groups are proportional to the degree of polymerization and, for the most part, are accessible from solution. HPGs and their derivatives have attracted significant attention in recent years due to their applications including drug-delivery,[6] polymer therapeutics[7,8] proteomics,[9,10] human serum albumin substitutes[11] and in other biomedical applications.[12,13] Although HPGs are less defined in terms of branching and polydispersity than perfectly branched dendrimers[1,14] their relative ease of synthesis and excellent biocompatibility profile[15–17] give this class of material a distinct advantage.

HPGs having molecular weight (M_w) up to 1 million have been synthesized overnight via a one-pot ring-opening polymerization of glycidol in sufficient quantities.[1,18] HPGs of either low (<30 kDa)[19] or high (>300 kDa)[18] M_ws with low polydispersity have been synthesized and investigated. However, one of the major drawback concerning the synthesis of HPGs has been the inability to synthesize well-defined medium M_w HPGs (50–300 kDa) using the simple ring-opening polymerization of glycidol. Since polydispersities of medium M_w HPGs (typically $2 < M_w/M_n < 10$) often exceed acceptable values the medium M_w HPGs have not been as extensively studied as that of low and high M_w fractions. Polymerization of less viscous, low M_w HPGs can be carried out in bulk, while low polydispersity very high M_w HPG can be synthesized using emulsions.[18] Considering the importance of hydrodynamic size and polydispersity of polymers in various material and biomedical applications, it is important that well-defined HPGs of all M_ws be available.[20,21] For instance, it is often critical that a well-defined polymer structure is needed to generate drug-conjugates to obtain consistent pharmacokinetic properties.[22] Also, it has been demonstrated that for proteomics technology applications and cell surface

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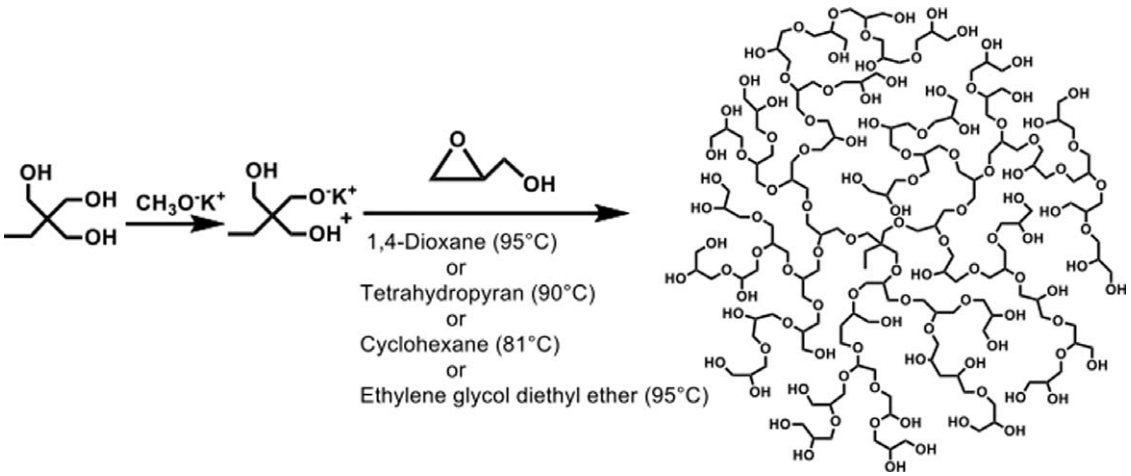


FIGURE 1 Schematic representation of HPG synthesized from TMP initiator in presence of different solvents.

modifications, the medium high M_w HPGs have distinct advantages.[9,10,23]

In this manuscript, we report a simple method for the synthesis of medium and high M_w HPGs with an emphasis on medium M_ws (50–300 kg/mol) with low polydispersity by anionic ring opening multibranching polymerization (ROMBP) with the assistance of different solvents. We studied the influences of various solvents, solvent to glycidol volume ratio, concentration of glycidol and the time of polymerization on the M_w and polydisperisty of the of HPGs formed. We have also studied the structural and solution properties of HPGs synthesized in different solvents.

EXPERIMENTAL

Materials and Methods

All the chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. Glycidol (96%) was purified by vacuum distillation and stored over molecular sieves in a refrigerator (4°C). The M_ws of the polymers were determined by gel permeation chromatography (GPC) using a DAWN-EOS multiangle laser light scattering (MALLS) (Wyatt Technology) and Optilab RI detectors in aqueous 0.1 N $NaNO_3$ solution: the details have been described elsewhere.[24]

^{1}H NMR and ^{13}CNMR spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer using D_2O as the solvent. Thermogravimetric analyses (TGA) was performed on a TGA Q500 (TA Instruments, Q series™). Samples were heated from 25 to 500°C at rate of 10°C/min.

Anionic ROMBP of Glycidol in Different Solvents

HPG was synthesized from glycidol via ROMBP in different solvents.[1,18] Briefly, in a three-necked round bottom flask, trimethylolpropane (TMP) (0.12 g, 92.8 mmol) was added to potassium methylate in methanol (25 wt %, 0.067 mL) under argon atmosphere. The mixture was stirred for 30 min, and excess methanol was removed under reduced pressure. The flask was flushed with argon, and a mechanical stirrer was fitted before placing the flask in an oil bath heated to 95°C. Required volume of 1,4-dioxane was added before the addition of monomer. Glycidol (12 mL) was added over a period of 8 h using a syringe pump and reaction continued for additional 7 h; the total polymerization time was 15 h unless otherwise mentioned. After the polymerization, the polymer was dissolved in methanol, neutralized by passing three times through a column packed with cation-exchange resin (Amberlite IRC-150). The polymer was then precipitated into excess of acetone and stirred for 2 h. Acetone was decanted out, and the procedure was repeated once more. In different experiments, the ratio of different solvents (1,4-dioxane, tetrahydropyran (THP), ethylene glycol diethyl ether (EGDE), cyclohexane and decane) to glycidol (solvent to glycidol ratio) and temperature were varied.

Solubility of HPGs Under Polymerization Conditions

Approximately 100 mg of HPGs (Mn—119 and 8.7 g/mol) was stirred with 5.0 mL of solvent (1,4-dioxane, THP, EGDE, cyclohexane and decane) at the polymerization temperature for each solvent for 15 h. After 15 h, supernatant was separated and TGA were performed to determine the concentration of polymer present in the supernatant.

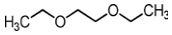
RESULTS AND DISCUSSION

Anionic ROMBP of glycidol from TMP using potassium methylate as the deprotonating agent was investigated in different solvents. The general synthetic scheme is shown in Figure 1. Solvents were selected based on their dielectric constants, boiling points, the presence or absence of oxygen in their chemical structure, and their cyclic or linear nature (Table 1). Different polymerization conditions were investigated to determine the effect of nature of solvents on M_w and polydispersity of HPGs synthesized.

Influence of Solvent and Solvent to Glycidol (S/G) Ratio

In first set of experiments, the effect of different solvents on ring opening polymerization of glycidol was investigated at constant amounts of TMP initiator, potassium methylate and reaction time (15 h) at a solvent to glycidol volume ratio 1.0. The M_w and polydispersity values obtained in different solvents are given in Table 1. A range of M_ws (5–540 kg/mol) obtained in

TABLE 1 Characteristics of Solvents and HPGs Synthesized in Different Solvents

Solvent[a]	Chemical structure	Dielectric constant[b]	$M_n \times 10^{-3}$ (g mol^{-1})[c]	PDI	Conversion (%)	Temperature (°C)
1,4-Dioxane		2.2	540	1.05	81	95
Tetrahydropyran		5.7	160	1.9	72	90
Cyclohexane		2.0	5.0	1.38	58	81
Ethylene glycol diethyl ether		5.1	48	2.1	61	95
Decane		2.0	10	1.6	59	95

[a] In all the polymerizations 12 mL of glycidol and 12.0 mL of solvents at solvent to glycidol ratio (S/G) 1 was used.
[b] Dielectric constant values obtained from literature (Ref. 30,31).
[c] Molecular weights and polydispersity index (PDI) were determined by GPC-MALLS in 0.1N $NaNO_3$. For all the polymerizations, trimethylolpropane (TMP) (0.125 g) and potassium methylate as a deprotonating agent were used. Conversion was measured from the weight of polymer obtained at the end of polymerization. Stirring rate during polymerization was 100 rpm in all cases. Polymerization time was 15 h in all cases.

different solvents at constant initiator to glycidol ratio illustrated the influence of solvents on the polymerization of glycidol. Polydispersity index was in the range 1.04–2.1 and the monomer conversion was 58–81%. Polymerization in 1,4-dioxane gave HPGs of highest M_w and lowest polydispersity index compared to other solvents. The M_ws of the HPG reported were after the precipitation in acetone. This might have removed very low M_w fragments typical of ROMBP of glycidol. Under the conditions studied, the polymerization occurred in two phases (heterogeneous conditions). The solvent acted as an emulsifier for the HPG formed in all the cases. Results given in Table 1 also suggest that the influence of dielectric constant of the solvents in the polymerization of glycidol might not have been as significant as previously been hypothesized.[18]

To further understand the influence of different solvents on ROMBP of glycidol, we investigated the influence of various solvent to glycidol (S/G) ratios at constant glycidol to initiator ratio. Results are given in Figure 2. As illustrated in Figure 2(A), the M_w of the HPG formed in different solvents showed dramatic changes with increase in S/G ratio. In 1,4-dioxane, the M_w of HPG formed increased moderately with increase in S/G ratio at low solvent content in the polymerization medium. However, the M_w of HPG increased dramatically with further increase in the 1,4-dioxane to glycidol ratio and it remained almost constant at very high M_w (~500 kg/mol). In the case of THP, there was a gradual increase in the M_w of the HPG formed with increase in S/G ratio and in EGDE, the M_w increase was much lower with increase in the amount of solvent. In cyclohexane, the M_w of HPG formed remained almost constant at all the ratios studied and only low M_w HPGs formed in the conditions studied. In all these cases, the M_w of HPG formed was higher than the theoretical M_w.

The polydispersities of the HPGs formed are shown in Figure 2(B). Except for EGDE, the polydispersity of HPGs decreased at higher S/G ratio. In 1,4-dioxane, very narrow PDI was achieved (~1.05). The PDI of HPG remained almost constant in cyclohexane at all S/G ratios studied. The data clearly demonstrate the influence of different solvents on polydispersity and it suggests that high S/G ratios were more suitable for achieving low polydispersities.

Representative GPC chromatograms of HPG formed in 1,4-dioxane and THP are shown in Figure 2(C,D) and Figure S1 (Supporting Information). As evident from the chromatograms, the bimodal M_w distribution of HPG formed was changed to a monomodal distribution with increase in S/G ratio. However, there was some dependence on the type of solvents used; in 1,4-dioxane, the monomodal distribution was achieved at lower S/G value than in THP. At lower S/G ratios, the polymerization was taking place in homogenous conditions (single phase) throughout the polymerization. However, with increase in S/G ratio, the polymerization was predominantly occurred under heterogeneous conditions (two phase). In polymerizations in 1,4-dioxane and THP, heterogeneous conditions produced high M_w HPG with narrow PDI. However, there was no such effect on the M_w of HPG formed in cyclohexane.

The solvent effect on M_w and polydispersity of HPG formed at different conditions may be due to several factors. In anionic ROMBP of glycidol, the rapid exchange of potassium cation between the hydroxyl groups is responsible for the branching as well as the uniform growth of the HPG[1,18] and it is anticipated that any change in the rapid exchange of cation may result in variation of such parameters. Unlike the case of bulk polymerization, the situation in polymerization in solvents can be quite different due to differences in the solvation of the growing alkoxide anion and the counter K^+ ion. This could possibly influence the nucleophilicity of the alkoxide anion and as well as the rapid exchange of K^+ ions between the hydroxyl groups thereby changing the polymerization behavior.

It has been reported that the solvation of ions can be influenced by the presence of interacting atoms or a group in the

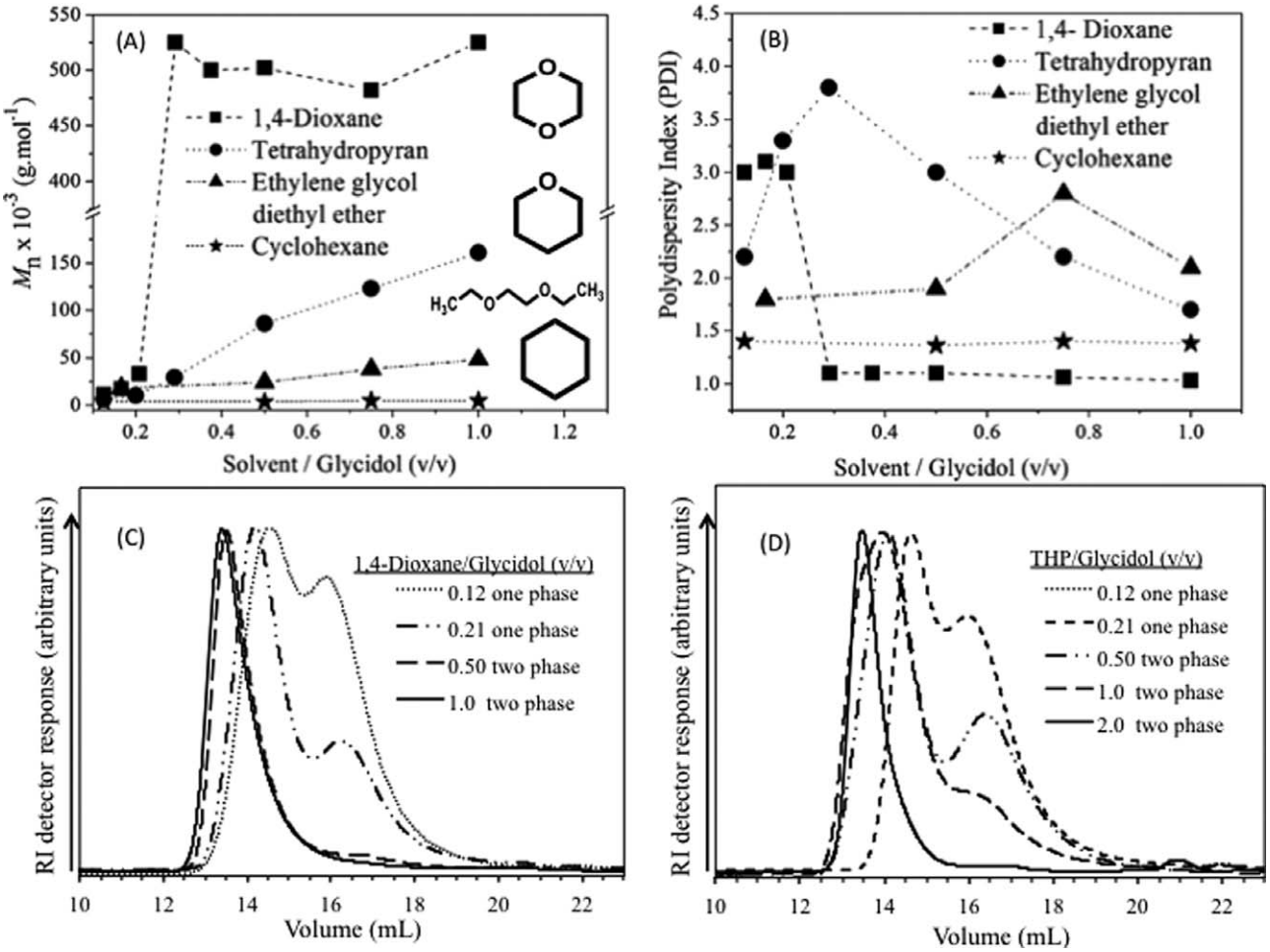


FIGURE 2 (A) Impact of different solvents on M_w of HPGs at constant initiator/glycidol ratio. (B) Effect of different solvents on the polydispersity of HPGs, at constant initiator/glycidol ratio (C) M_ws distributions of HPGs formed in different 1,4-dioxane/glycidol ratios at constant initiator/glycidol ratio. (D) M_w distributions of HPGs obtained in different THP/glycidol ratios at constant initiator/glycidol ratio. M_w characteristics determined by GPC-MALLS in 0.1 N $NaNO_3$. Glycidol (12.0 mL), TMP (0.125 g) and polymerization time (15 h).

solvent. In the present case, 1,4-dioxane, THP and EGDE have oxygen atoms in the structure and could interact with the growing anion as well as the K^+ ion. It is known that K^+ ions are more solvated than the anions due to the stronger electrostatic interaction between the exposed negative end of the dipole on the oxygen atom of solvent and the cation.[25] The solvation of K^+ is best described in terms of the electrostatic interaction between the ion and polar solvent molecules similar to other simple spherical univalent cations with closed electron shells.[26] The interaction of K^+ ions with solvents will also depend on the chemical structure of solvents and on the number of oxygen atoms present in the structure. Thus, it is anticipated that the solvents with more oxygen atoms can have better solvation power than one with a lower number of oxygen atoms. Such interactions with solvent molecules could possibly slow down the exchange reaction of K^+ ions between different hydroxyl groups in HPG during the polymerization. Such interactions could also possibly increase the nucleophilicity of the anion.[27] Iijima et al.[28] have shown that the interaction of potassium cation with solvent can influence the reactivity of oxonium anion in the anionic polymerization of 2-(t-butyldimethylsiloxyethyl) methacrylate. Increased anion nucleophilicity could enhance the nucleophilic ring opening reaction of glycidol in the propagation step resulting in an increased M_ws.

In the present case, 1,4-dioxane has two oxygen atoms and THP has one oxygen atom in the structure. Therefore we anticipated that the K^+ cation will have a stronger interaction with 1,4-dioxane than with THP resulting in increased nucleophilicity of the alkoxide anion[27] as well as a decrease in exchange rate of K^+ ions. Both these factors can enhance the M_w HPGs in 1,4-dioxane than THP (Table 1, Fig. 2). The relatively weaker interactions of THP with anion and cations compared to 1,4-dioxane may be responsible for the better control of the M_w of HPG produced in this solvent. Cyclohexane and decane do not have any interaction with the K^+ ions due to the absence of oxygen atoms in these molecules and therefore have no effect on the polymerization (Fig. 2). EGDE also has two oxygen atoms similar to 1,4-dioxane,

TABLE 2 Solubility of HPGs in Different Solvents[a]

	1,4-dioxane (95 °C)	THP (88 °C)	EGDE (95 °C)	Cyclohexane (81 °C)	Decane (95 °C)
HPG ((Mn-119 kg/mol)					
Solubility (mg/mL)	6.2	3.81	1.90	1.2	–
HPG (Mn-8.7 kg/mol)					
Solubility (mg/mL)	7.4	6.2	2.0	1.6	–

[a] Experimental conditions: 100mg of HPG (119 kDa, 8.70 kDa) was stirred for with solvents (5.0 mL at polymerization temperature. Supernatant was collected and the amount of HPG solubilized in the solvents was determined using thermogravimetric analyses (TGA). This information was used for determining the solubility.

however, the M_w of the HPG formed was not changed considerably with increase in S/G ratio. This could be due to the differences in exposure of oxygen atoms present in 1,4-dioxane and tertahydropyran compared to the EGDE[27,29] which provides better interaction with the K^+ cation and increased nucleophilicity of the alkoxide anion. The change in the M_w of HPG formed in EGDE compared to that formed in cyclohexane and decane illustrates the influence of solvent-cation interaction in these polymerizations.

Another parameter, which might be influencing the polymerization, is the difference in the solubility of HPG in solvents used for polymerization. This parameter is expected to influence the formation of homogenous or heterogeneous phases during polymerization. The formation of heterogeneous phase may change the accessibility of the growing anion to glycidol thereby changing the uniform growth of the polymer. Thus we determined the solubility of high M_w HPG (Mn-119 kg/mol) and low M_w HPG (Mn-8.7 kg/mol) in the solvents used for polymerization at the reaction temperature. Polar solvents such as 1,4-dioxane, THP and EGDE showed some solubility when HPG was stirred for 15 h at the reaction temperature (Table 2) compared to non-polar solvents. Generally, solvents which showed higher solubility for HPG (1,4-dioxane and THP) gave higher M_w than poor solvents (Fig. 2 and Table 2). For instance, HPG was more soluble in 1,4-dioxane and the polymerization in this solvent gave the highest M_w HPGs. Also in this solvent, the PDI was lower possibly due to more uniform growth of HPG in the solution phase due to its higher solubility (Fig. 2). The anionic ROMBP of glycidol in DMF and DMSO resulted in brownish products and was not investigated further.

Effect of Glycidol Concentration at Constant Solvent to Glycidol Ratio

We further investigated the influence of monomer concentration on the M_w and PDI of HPG formed at constant S/G ratio in 1,4-dioxane and THP. A constant amount of initiator was used, thus the initiator to monomer ratio was changed. Figure 3 shows the results from this set of experiments. Figure 3(A,B) give the data from the polymerization in 1,4-dioxane and Figure 3(C,D) give the results from the polymerization in THP. In these solvents the polymerization phase changed to heterogeneous with time. With increase in glycidol concentration, the M_w of the HPG formed gradually increased in both 1,4-dioxane and THP. The PDI decreased with increase in glycidol amount in the case of 1,4-dioxane giving values lower than 1.1 in some cases. The GPC chromatograms show that a monomodal distribution was achieved in 1,4-dioxane [Fig. 3(B), Supporting Information Fig. S2]. In the case of THP, the PDI increased initially and then decreased with increase in glycidol amount. The bimodal distribution of M_ws was observed initially but the distribution changed to monomodal with increase in glycidol content [Fig. 3(D), Supporting Information Fig. S2]. A range of M_ws of HPGs was produced with relatively low PDI (1.1 to 1.5) [Fig. 3(A,C)] under selected conditions. Importantly we were able to produce HPGs with M_ws in the range 30–500 kg/mol either by changing the solvents for polymerization or by changing the glycidol concentration.

Effect of Polymerization Time at Constant Initiator to Glycidol and Solvent to Glycidol Ratios

To further investigate the glycidol polymerization behavior, the effect of polymerization time on M_ws of HPG formed in 1,4-dioxane at constant initiator/glycidol and solvent/glycidol ratio was determined. The solvent to glycidol ratio was kept at 0.2. It was shown earlier that at similar S/G ratio resulted in bimodal distribution of M_ws when the polymerization was terminated at 15 h [Fig. 2(C)]. As shown in Figure 4(A), the M_ws of HPG increased with increase in polymerization time with decrease in polydispersity [Fig. 4(B)]. It is evident from the GPC chromatogram that the low M_w fraction was decreased considerably with increase in polymerization time. Similar effects were also noticed in case of THP and EGDE (Table 3). The time required for full conversion of monomer depends on the amount and type of solvent.

Physicochemical Properties of HPGs Synthesized in Different Solvents

Degree of Branching

The degree of branching of HPGs synthesized in different solvents was determined by using inverse gated (IG) ^{13}C NMR spectroscopy.[1,18] Different M_w HPGs were used for this analysis. The degree of branching was calculated from different structural units of HPG reported by Sunder et al.[1] (Fig. S3, Supporting Information). Our results show that HPG synthesized in 1,4-dioxane, THP and EGDE gave similar degrees of branching (0.561, 0.575 and 0.585 respectively) for

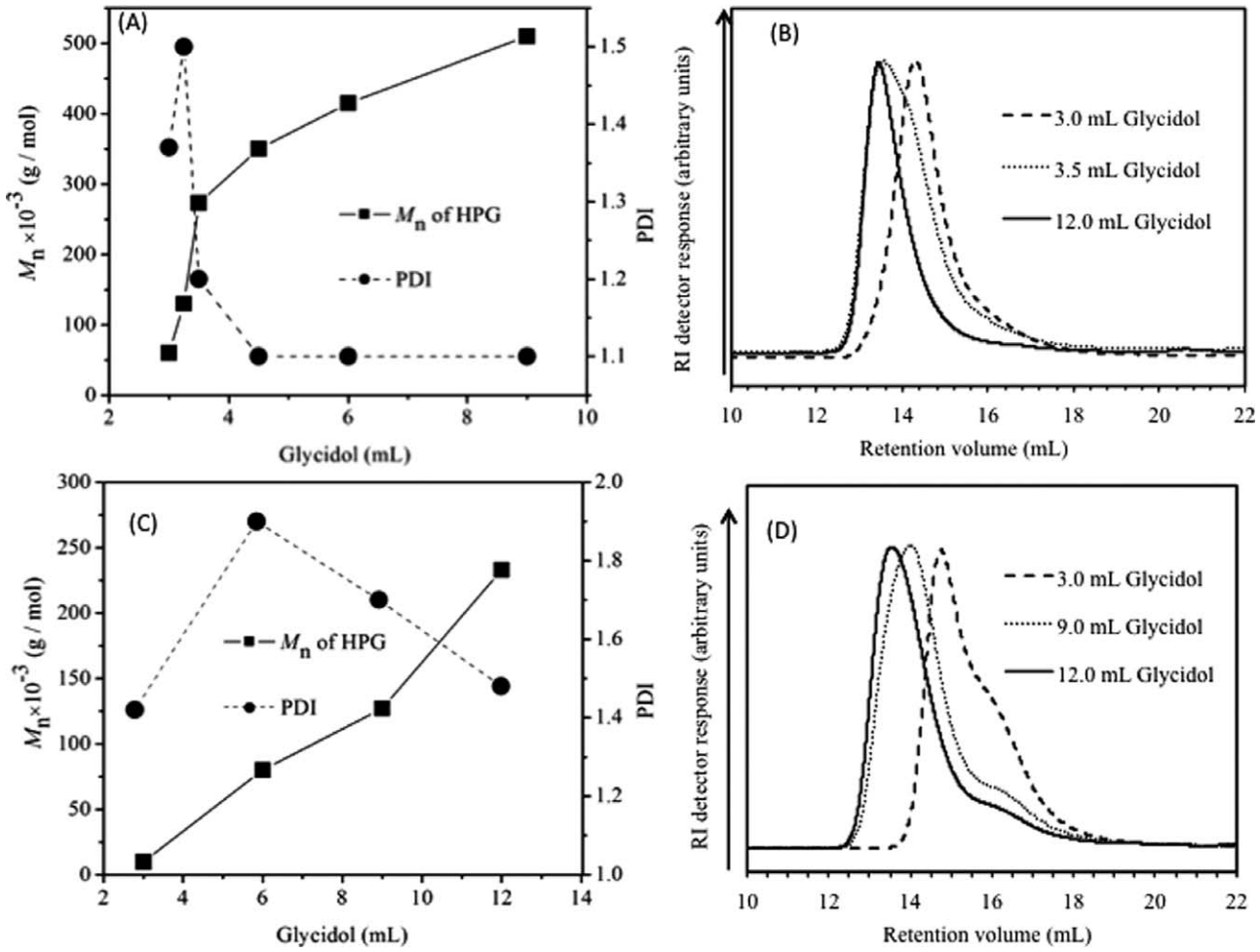


FIGURE 3 (A) Effect of glycidol concentration on M_w and polydispersity of HPGs at constant 1,4-dioxane/glycidol ratio (~1.50). (B) M_w distributions of HPGs obtained with different glycidol concentrations at constant 1,4-dioxane/glycidol ratio. (C) Effect of glycidol concentration on M_ws and polydispersity of HPGs at constant THP/glycidol ratio (~1.50). (D) M_w distributions of HPGs obtained with different glycidol concentrations at a constant THP/glycidol ratio. M_w characteristics determined by GPC-MALLS in 0.1 N $NaNO_3$, TMP (0.125 g) and polymerization time (15 h), solvent/glycidol ~1.50.

polymers having M_w around 100kDa (Supporting Information Table S1).

As there were only slight difference observed in the degree of branching and no trends emerged, it can be concluded that the microstructure of the HPGs prepared in different solvents is similar. However, there was a slight difference in the relative abundance of different structural units present within HPGs synthesized in different solvents; the ratio of linear 1,3 (L_{13}) and linear 1,4 (L_{14}) units was different (Supporting Information Fig. S3 and Table S2). Higher L_{13} to L_{14} ratio was observed for 1,4-dioxane(1:3.7) compared to THP(1:2.9) and EGDE (1:2.5) indicated the higher counter ion exchange rate in 1,4-dioxane compared to other solvents. High M_w and low M_w HPGs (8 and 500 kDa) also showed similar trend in 1,4-dioxane, THP and EGDE(Table S2, Supporting Information). The large difference between linear 1,3 and linear 1,4 units in HPG prepared in different solvents could be due to the differences in the reactivity of primary and secondary alkoxide ions. The formation of L_{13} was from secondary alkoxides where as L_{14} was from primary alkoxides group. This data also support the fact that although M_w and PDI changed with solvent conditions, the solvent interaction is not changing the propagation steps originally proposed.[1]

Thermal Properties

The HPGs prepared in different solvents were analyzed by thermogravimetric analysis (TGA). The change in the thermal stability of a polymer is often caused by changes in the structure of the repeat unit or polymer as a whole (e.g., degree of branching, chain length). HPGs synthesized in three different solvents (1,4-dioxane, THP, EGDE) with similar M_w (300 kDa) showed no significant difference in thermal stability (Supporting Information Fig. S4). As, the interactions between the individual globular, hyperbranched polymers remained more or less consistent, it is possible to deduce that the physical properties of the bulk material do not change. In conjunction with

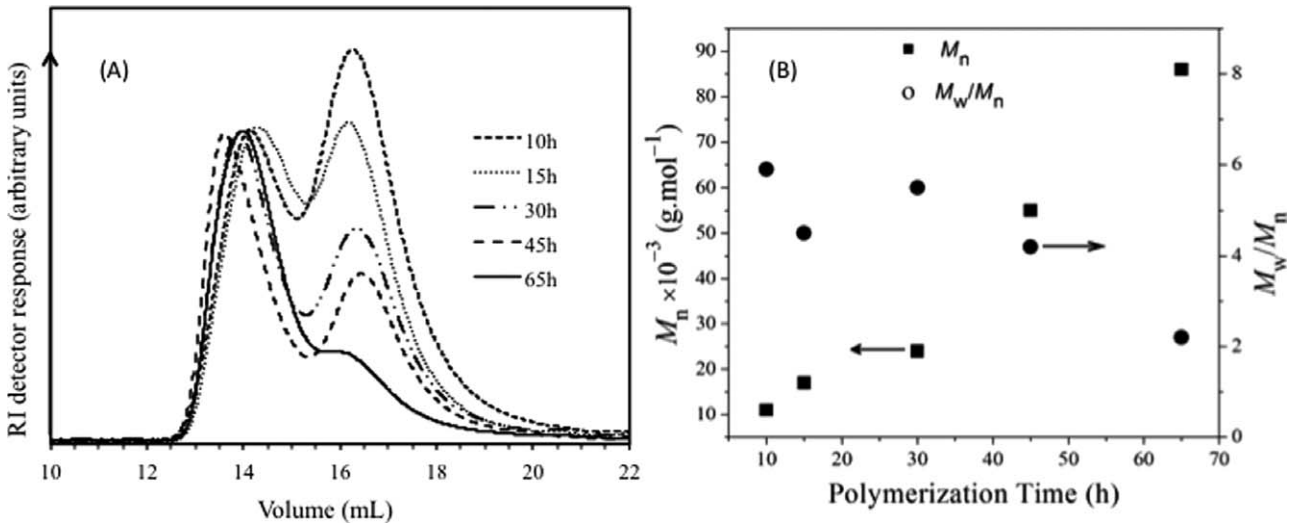


FIGURE 4 (A) M_w distribution of polymers obtained with increasing reaction time with similar concentrations of 1, 4-dioxane. (B) M_w of polymers and their polydispersity with increasing reaction time. Glycidol 12.0 mL; 1,4-dioxane 2.5 mL; 0.125 g of TMP and 95 °C were used for all the polymerizations.

the NMR data and the thermal stability data, we confirmed that the structural characteristics of these hyperbranched polymers do not alter significantly when prepared in different solvents. Results suggest that there were no major differences in the degradation pattern of the HPGs prepared in different solvents.

Solution Properties of HPGs

Solution properties of HPGs synthesized in different solvents were also analyzed. The intrinsic viscosity values were determined by a triple detector system consist of a refractive index detector, light scattering detector, and a viscosity detector (Viscotek Corp). The radius of gyration (R_g) and hydrodynamic radii (R_h) of the polymers were extracted from the viscosity data, while the hydrodynamic radii (R_h) were obtained from the QELS detector (Wyatt Technology Corp). The low intrinsic viscosity values suggest the compact structure of the HPG synthesized in different solvents (Supporting Information Table S3). The ratio R_g/R_h can be used to determine the extent of molecular compactness of a polymer. In agreement with previously reported values of for high M_w HPG,[18] the R_g/R_h values for the current set of polymers are around 1.3 and are indicative of hyperbranched structures. Importantly, the consistency of the R_g/R_h values indicates that the nature of branching within each polymer is similar, irrespective of the solvent used for polymerization.

CONCLUSIONS

Well-defined medium M_w HPGs (50–300 kDa) cannot be routinely synthesized using existing ring opening anionic polymerization of glycidol. We have described a method for the synthesis of medium to high M_w HPGs (50–540 kDa) using a solvent interaction mechanism. The M_w and polydispersity of the HPG formed dependent on the nature of the solvents, solvent to glycidol volume ratio, concentration of glycidol and the time of polymerization. Selected polymerization conditions produced medium to high M_w HPGs with relatively low PDI. Solvents with more oxygen atoms and cyclic structure have more effect on M_w than their cyclic analogue without oxygen. The solvent effect is attributed to the increased solvation of the potassium cation in certain solvents which increased the nucleophilcity of the alkoxide anion. The M_w and polydispersity of the HPGs were significantly affected by the nature of the polymerization phase (homogeneous or heterogeneous) and solubility of the HPG. The solvent interaction during the polymerization did not change the microstructure of the polymers formed in different solvents. The

TABLE 3 Effect of Polymerization Time on Molecular Weights of Polymers[a]

S. No.	Solvent (mL)	Glycidol (mol)	Time (h)	$M_n \times 10^{-3}$ g mol^{-1} [a]	PDI	Conversion (%)
1	THP (4.5)	0.040	15	9	1.3	56
2	THP (4.5)	0.040	45	12	1.7	65
3	EGDE (12.0)	0.162	15	48	2.1	60
4	EGDE (12.0)	0.162	45	78	3.6	65

[a] Molecular weights and polydispersity index (PDI) were determined by GPC-MALLS in 0.1N $NaNO_3$. For all the polymerizations, trimethylolpropane (TMP) (0.125 g) and potassium methylate as a deprotonating agent were used. Polymerization temperature was 95 °C, under argon atmosphere. Conversion was measured from the weight of polymer obtained at the end of polymerization.

structure and physical properties of the HPGs, regardless of M_w or polymerization batch, did not change significantly. Thermal characterization of polymers formed in different solvents did not show any change in degradation pattern of HPG. IG ^{13}C NMR spectroscopy of the different polymers indicated that the degree of branching and overall structure of the hyperbranched polymer did not vary with type of solvents.

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