

Synthesis and Characterization of Bio-based Alkyl Terminal Hyperbranched Polyglycerols: A Detailed Study of Their Plasticization Effect and Migration Resistance

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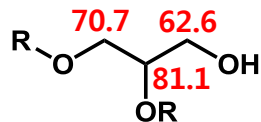
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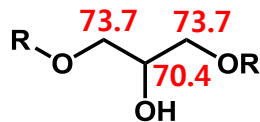
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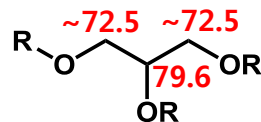
Respective ^{13}C NMR shifts of structural units



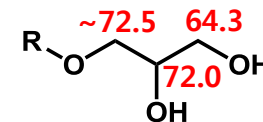
Linear 1,3 (L_{13})



Linear 1,4 (L_{14})



Dendritic (D)



Terminal (T)

Sample	L_{13} (%)	L_{14} (%)	D (%)	T (%)	DB
HPG3	8.2	36.0	10.9	44.9	0.329
HPG9	10.0	34.1	16.5	39.3	0.429
HPG21	10.2	32.9	20.4	36.4	0.486

Degree of branching (DB)

$$DB = \frac{2D}{2D + L_{13} + L_{14}}$$

Ref. *macromolecules*. 1999, 32, 4240.

Fig. S1 The Respective ^{13}C NMR shifts and the relative percentages of L_{13} , L_{14} , D, and T units

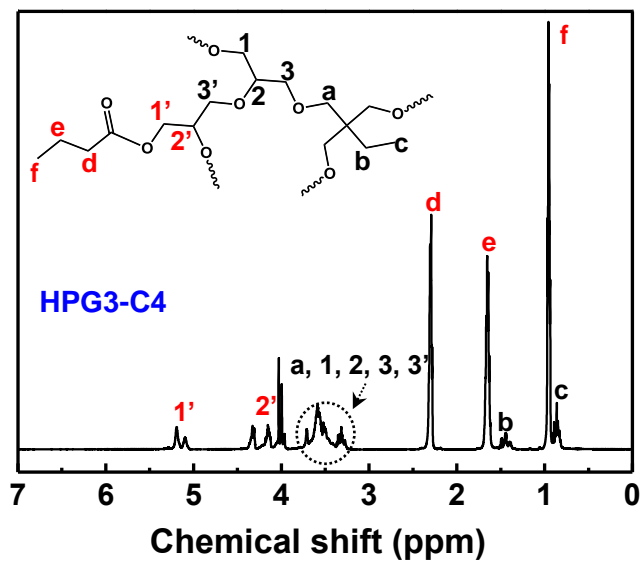
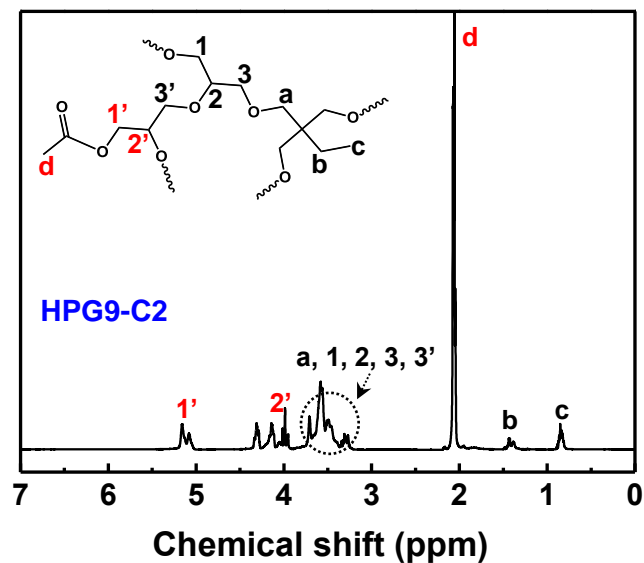
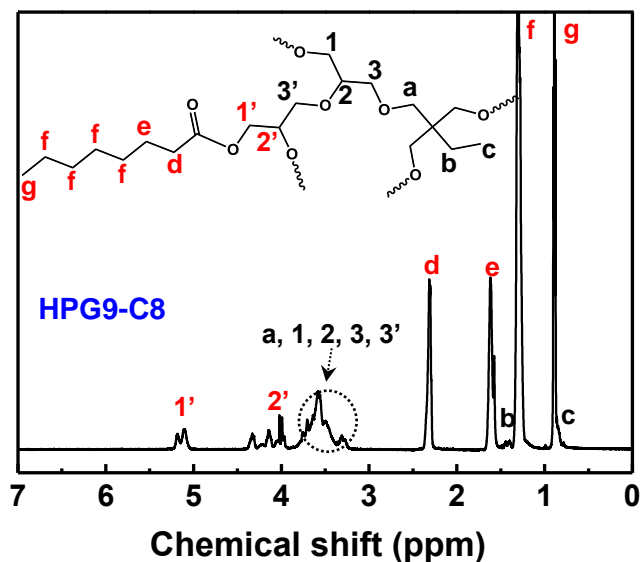
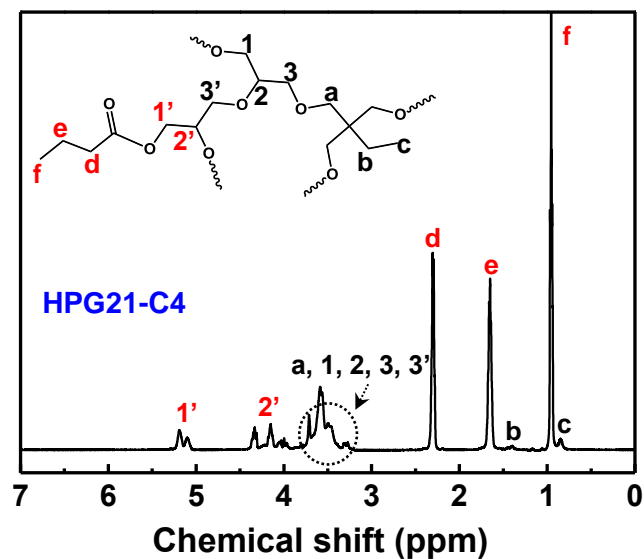
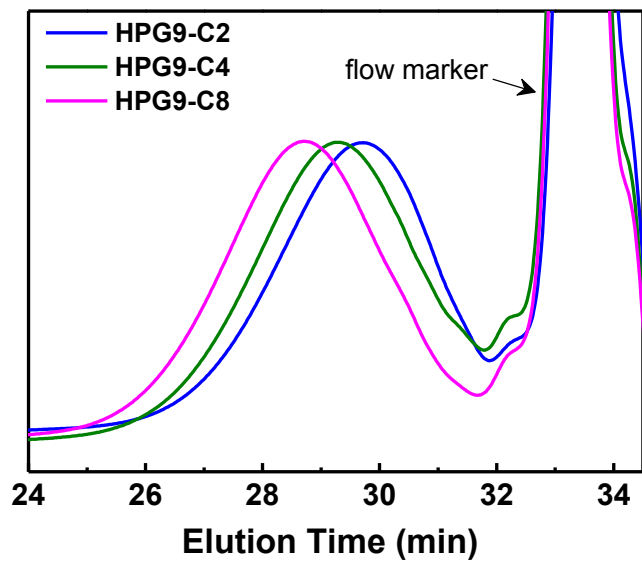
(a)**(b)****(c)****(d)**

Fig. S2 ^1H NMR spectra for the alkyl-HPGs (a) HPG3-C4, (b) HPG9-C2, (c) HPG9-C8, and (d) HPG21-C4

(a)



(b)

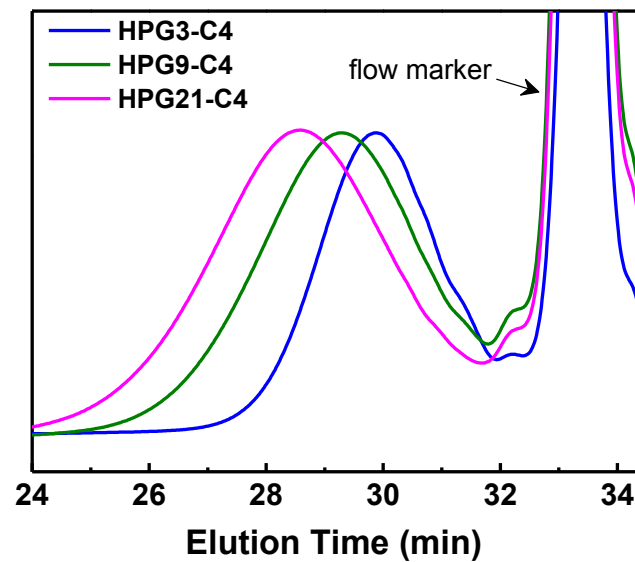


Fig. S3 SEC curves for the alkyl-HPGs (a) HPG9-C2, HPG9-C4, and HPG9-C8 (b) HPG3-C4, HPG9-C4, and HPG21-C4

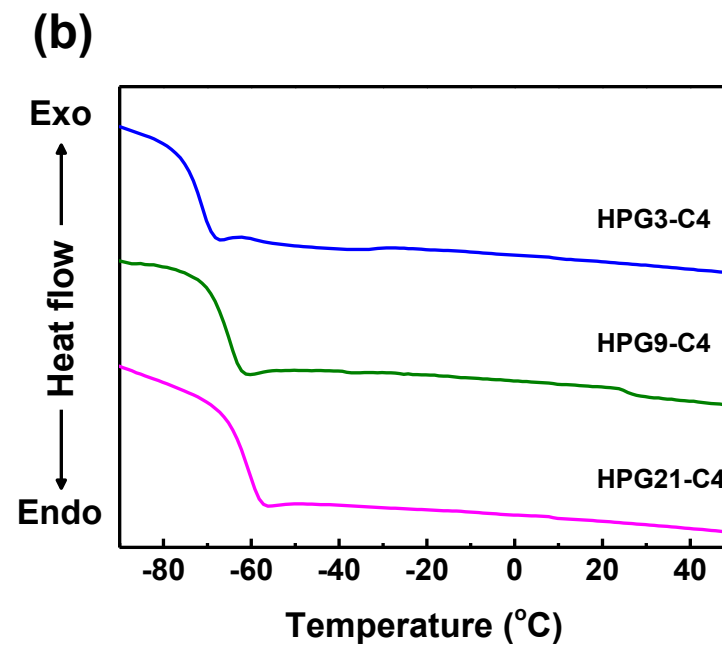
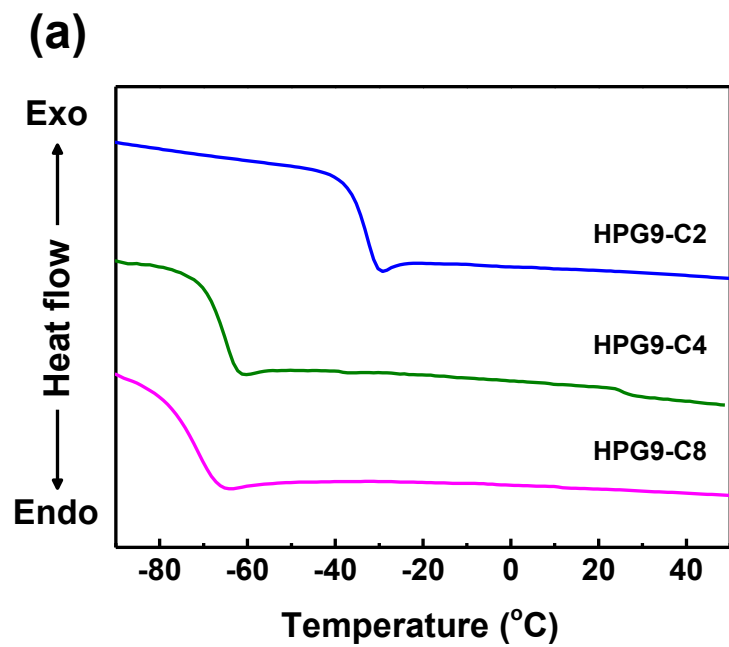
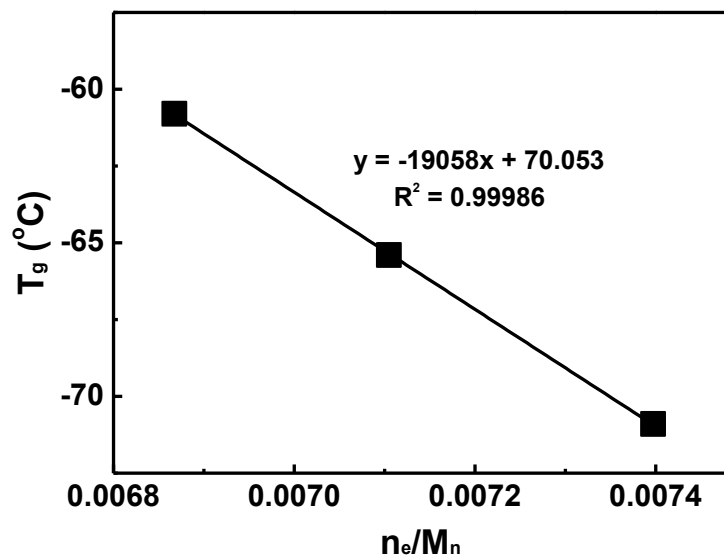


Fig. S4 DSC curves for the alkyl-HPGs (a) HPG9-C2, HPG9-C4, and HPG9-C8 (b) HPG3-C4, HPG9-C4, and HPG21-C4



Chain ends-free volume theory

$$T_{g, \text{dend}} = T_{g, \infty} - \frac{n_e \times K}{M_n}$$

K : a constant, individual for each polymer

n_e : the number of end groups

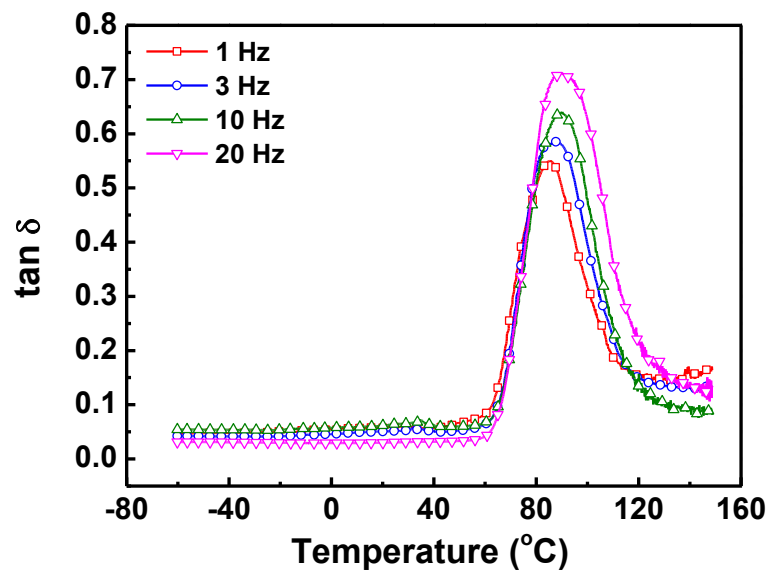
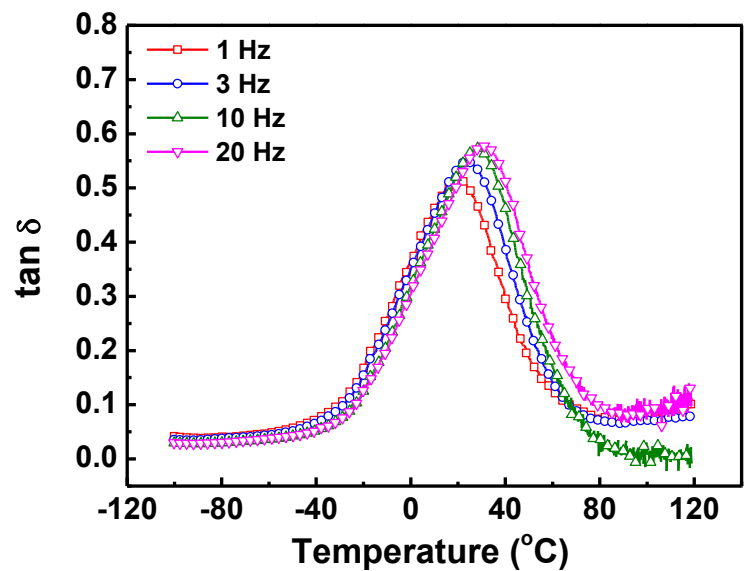
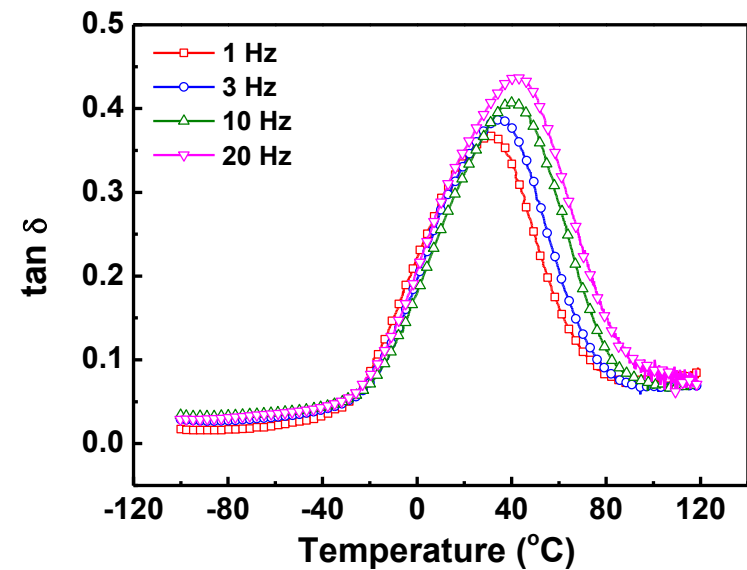
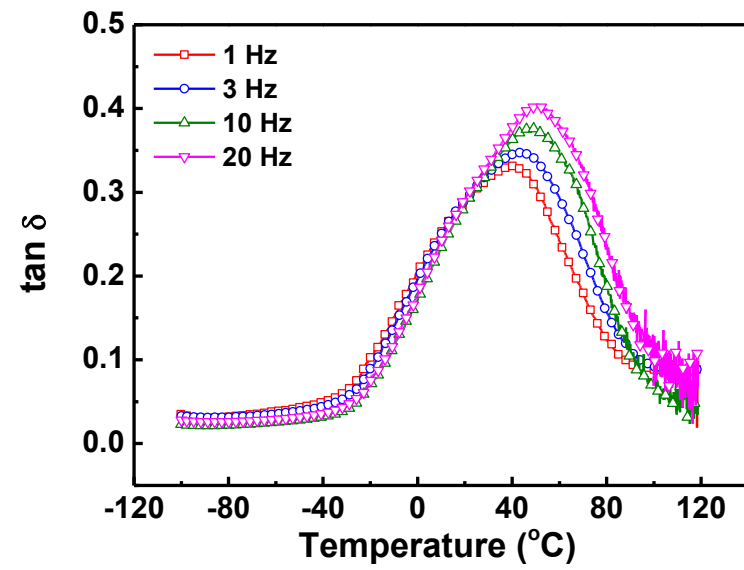
Ref. *macromolecules*. **1993**, 26, 1514.

Fig. S5 The change of T_g according to the n_e/M_n for HPG-C4 series

Table S1 The calculated solubility parameters for the HPGs and alkyl-HPGs

Factor	HPG3-C4	HPG9-C2	HPG9-C4	HPG9-C8	HPG21-C4	HPG3	HPG9	HPG21
DP of glycidol	3.078	9.018	9.018	9.018	20.880	3.078	9.018	20.880
# of CH ₂	21.27874	22.036	44.75002	88.66379	90.27232	10.156	22.036	45.76
# of CH	3.078	9.018	9.018	9.018	20.88	3.078	9.018	20.88
# of CH ₃	6.56137	12.50123	12.35701	12.10463	23.25616	–	–	–
# of O	3.078	9.018	9.018	9.018	20.88	3.078	9.018	20.88
# of COO	5.56137	11.50123	11.35701	11.10463	22.25616	–	–	–
# of OH	0.51663	0.51677	0.66099	0.91337	1.62384	6.078	12.018	23.88
M _{n,NMR} (g mol ⁻¹)	752	1286	1598	2204	3241	362	802	1681
Sum of G (cal ^{1/2} cm ^{3/2} mol ⁻¹)	6259.874	10055.19	13000.59	18708.88	25928.69	3697.762	8325.022	17565.52
Density (g cm ⁻³)	1.06	1.10	1.08	0.98	1.09	1.22	1.22	1.23
δ (cal ^{1/2} cm ^{3/2})	8.93	8.67	8.85	8.38	8.80	12.46	12.66	12.85
Δδ (cal ^{1/2} cm ^{3/2})	0.73	0.99	0.81	1.28	0.86	2.80	3.00	3.19

- G values for CH₂, CH, CH₃, O, COO and OH are 214, 133, 28, 70, 310 and 148 (cal^{1/2} cm^{3/2} mol⁻¹), respectively.
- Δδ (Difference in solubility parameter) = |δ_{PVC} – δ_{plasticizer}|

(a)**(b)****(c)****(d)**

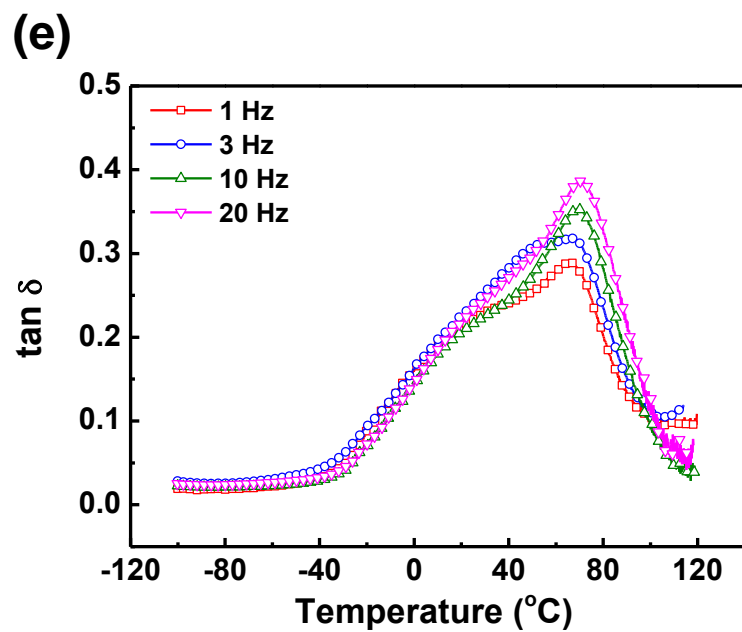


Fig. S5 The frequency dependence of the tan δ peak temperatures (a) neat PVC, (b) PVC/DEHP, (c) PVC/HPG3-C4, (d) PVC/HPG9-C4, and (e) PVC/HPG21-C4

Table S2 Acute toxicity group summary for (a) HPG3-C4

(i)

Group	Dose (mg/kg B.W.)	Mortality	
		Male	Female
G1	0	0% (0 / 5) ^a	0% (0 / 5)
G2	1330	0% (0 / 5)	0% (0 / 5)
G3	2000	0% (0 / 5)	0% (0 / 5)
G4	3000	0% (0 / 5)	0% (0 / 5)

^a : No. of dead animals / No. of tested animals

(iii)

Unit : g

Group	Dose (mg/kg B.W.)	Sex	Days after administration			
			0	7	14	
G1	0	Male	Mean	162.9	248.5	308.5
			S.D.	4.7	13.9	19.5
			N	5	5	5
		Female	Mean	126.0	174.7	190.9
			S.D.	5.1	5.5	16.6
			N	5	5	5
G2	1330	Male	Mean	165.5	249.7	306.7
			S.D.	5.7	14.0	10.1
			N	5	5	5
		Female	Mean	125.0	171.4	205.8
			S.D.	6.8	9.5	14.5
			N	5	5	5
G3	2000	Male	Mean	165.2	243.4	308.7
			S.D.	4.5	7.4	11.2
			N	5	5	5
		Female	Mean	125.6	174.8	201.7
			S.D.	10.8	16.2	24.4
			N	5	5	5
G4	3000	Male	Mean	165.9	254.5	289.6
			S.D.	2.1	10.8	21.2
			N	5	5	5
		Female	Mean	125.7	178.2	213.1
			S.D.	8.1	14.9	9.4
			N	5	5	5

N : Number of animals, S.D. : Standard deviation

(ii)

Group	Dose (mg/kg B.W.)	Sex	Number of animal	Clinical signs
Female	5	Normal		
G2	1330	Male	5	Normal
		Female	5	Normal
G3	2000	Male	5	Normal
		Female	5	Normal
G4	3000	Male	5	Normal
		Female	5	Normal

(iv)

Findings		Group (mg/kg B.W.)							
		G1 (0)		G2 (1330)		G3 (2000)		G4 (3000)	
		Male	Female	Male	Female	Male	Female	Male	Female
Number of animals		5	5	5	5	5	5	5	5
Gross findings	No gross findings	5	5	5	5	5	5	5	5
Internal findings	No gross findings	5	5	5	5	5	5	5	5

(i) Mortality, (ii) Clinical signs,

(iii) Body weight, (iv) Necropsy findings

Table S2 Acute toxicity group summary for (b) HPG9-C4

(i)

Group	Dose (mg/kg B.W.)	Mortality	
		Male	Female
G1	0	0% (0 / 5) ^a	0% (0 / 5)
G2	1330	0% (0 / 5)	0% (0 / 5)
G3	2000	0% (0 / 5)	0% (0 / 5)
G4	3000	0% (0 / 5)	0% (0 / 5)

^a : No. of dead animals / No. of tested animals

(iii)

Unit : g

Group	Dose (mg/kg B.W.)	Sex	Days after administration			
			0	7	14	
G1	0	Male	Mean	167.3	255.8	304.4
			S.D.	15.1	24.8	19.8
			N	5	5	5
		Female	Mean	120.6	170.1	197.0
			S.D.	4.2	13.4	4.8
			N	5	5	5
G2	1330	Male	Mean	164.6	253.3	306.5
			S.D.	10.9	8.5	25.2
			N	5	5	5
		Female	Mean	126.1	176.8	192.8
			S.D.	6.1	11.4	9.6
			N	5	5	5
G3	2000	Male	Mean	158.4	246.9	292.5
			S.D.	6.9	12.5	25.5
			N	5	5	5
		Female	Mean	127.2	175.0	199.1
			S.D.	8.3	19.3	14.3
			N	5	5	5
G4	3000	Male	Mean	153.9	235.6	305.0
			S.D.	4.1	13.7	25.0
			N	5	5	5
		Female	Mean	129.8	183.7	202.7
			S.D.	7.4	5.4	15.4
			N	5	5	5

N : Number of animals, S.D. : Standard deviation

(ii)

Group	Dose (mg/kg B.W.)	Sex	Number of animal	Clinical signs
G1	0	Male	5	Normal
		Female	5	Normal
G2	1330	Male	5	Normal
		Female	5	Normal
G3	2000	Male	5	Normal
		Female	5	Normal
G4	3000	Male	5	Normal
		Female	5	Normal

(iv)

Findings		Group (mg/kg B.W.)							
		G1 (0)		G2 (1330)		G3 (2000)		G4 (3000)	
		Male	Female	Male	Female	Male	Female	Male	Female
Number of animals		5	5	5	5	5	5	5	5
Gross findings	No gross findings	5	5	5	5	5	5	5	5
Internal findings	No gross findings	5	5	5	5	5	5	5	5

(i) Mortality, (ii) Clinical signs,

(iii) Body weight, (iv) Necropsy findings

Table S2 Acute toxicity group summary for (c) HPG21-C4

(i)

Group	Dose (mg/kg B.W.)	Mortality	
		Male	Female
G1	0	0% (0 / 5) ^a	0% (0 / 5)
G2	1330	0% (0 / 5)	0% (0 / 5)
G3	2000	0% (0 / 5)	0% (0 / 5)
G4	3000	0% (0 / 5)	0% (0 / 5)

^a : No. of dead animals / No. of tested animals

(iii)

Unit : g

Group	Dose (mg/kg B.W.)	Sex	Days after administration			
			0	7	14	
G1	0	Male	Mean	171.5	258.4	317.6
			S.D.	12.1	13.7	23.1
			N	5	5	5
		Female	Mean	122.8	171.7	195.4
			S.D.	9.6	17.5	22.0
			N	5	5	5
G2	1330	Male	Mean	167.1	253.5	309.0
			S.D.	10.2	16.5	23.3
			N	5	5	5
		Female	Mean	125.4	173.4	196.0
			S.D.	8.4	10.1	11.7
			N	5	5	5
G3	2000	Male	Mean	171.6	258.3	309.8
			S.D.	5.9	10.1	23.1
			N	5	5	5
		Female	Mean	117.1	167.3	192.1
			S.D.	5.8	11.5	16.9
			N	5	5	5
G4	3000	Male	Mean	167.6	255.7	320.5
			S.D.	10.2	12.8	19.9
			N	5	5	5
		Female	Mean	125.3	177.7	203.4
			S.D.	8.3	11.1	12.8
			N	5	5	5

N : Number of animals, S.D. : Standard deviation

(ii)

Group	Dose (mg/kg B.W.)	Sex	Number of animal	Clinical signs
G1	0	Male	5	Normal
		Female	5	Normal
G2	1330	Male	5	Normal
		Female	5	Normal
G3	2000	Male	5	Normal
		Female	5	Normal
G4	3000	Male	5	Normal
		Female	5	Normal

(iv)

Findings	Group (mg/kg B.W.)	Group (mg/kg B.W.)							
		G1 (0)		G2 (1330)		G3 (2000)		G4 (3000)	
		Male	Female	Male	Female	Male	Female	Male	Female
Number of animals		5	5	5	5	5	5	5	5
Gross findings	No gross findings	5	5	5	5	5	5	5	5
Internal findings	No gross findings	5	5	5	5	5	5	5	5

(i) Mortality, (ii) Clinical signs,

(iii) Body weight, (iv) Necropsy findings