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Theoretical analysis of the reaction between equivalent quantities of sec-butyllithium and *m*-divinylbenzene

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This paper deals with the theoretical aspect of the reaction between sec-butyllithium and equivalent quantities of *m*-diisopropenylbenzene. The expression of various molecular parameters of the resulting adducts, such as the molecular weight distribution function, the number- and the weight-average molecular weights, the functionality distribution and the average functionality, are given. By the aid of these expressions, we can gain insight into the reaction process. When the reaction is close to completion, precipitation is usually observed because $x = 1$ is the critical condition of the gelation for this reaction system, where x is the conversion of double bonds. In the meantime, the average functionality approaches 2 even though 37% of the sec-butyllithium initially added to the system remains unreacted and joins in the monofunctional adduct at the end of the reaction. In general, the theoretical results are in agreement with the experimental data reported by Cameron and Buchan (*Polymer*, 1979, **20**, 1129). © 1997 Elsevier Science Ltd.

(Keywords: sec-butyllithium; *m*-diisopropenylbenzene; molecular weight distribution; critical condition of gelation)

Introduction

The reaction of equivalent quantities of sec-butyllithium with *m*-divinylbenzenes was reported as an effective approach for the preparation of a bifunctional anionic initiator[1–6]. Authors[2,6] usually used *m*-diisopropenylbenzene as a favourable precursor to avoid competition between the metallation and the homopolymerization because of the low ceiling temperature. The existence of a catalytic amount of triethylamine in the reaction system also led to the formation of the diadduct. On the other hand, some experimental data indicated that this reaction may not be a good route to the synthesis of a bifunctional initiator of anionic polymerization. For example, *m*-diethenylbenzene is partially oligomerized[7], whereas a bimodel molecular weight distribution is observed for the polymers prepared from the *m*-bis(1-phenylethenyl)benzene adduct[8]. Moreover, Cameron and Buchan[9] claimed that the reaction of *m*-diisopropenylbenzene with an equivalent quantity of sec-butyllithium, in benzene or cyclohexane, results in a mixture of di- and poly-functional compounds, together with the unreacted sec-butyllithium, rather than in a bifunctional initiator, even at 55°C and in the presence of triethylamine. In addition, precipitation usually occurs when the reaction of *m*-diisopropenylbenzene with an equivalent amount of sec-butyllithium is close to completion[10]. These experimental phenomena seem in support of the argument of Cameron and Buchan[9]. Up to now, a considerable effort has been devoted to the synthesis of the hydrocarbon soluble bifunctional organolithium compounds and to the related mechanism[8,10,11]. The investigation of the theoretical aspect of the reaction between equivalent quantities of *m*-divinylbenzene and sec-butyllithium may facilitate the understanding of the reaction process.

Molecular parameters of the adducts

Here, we confine ourselves to dealing with the reaction between equivalent quantities of sec-butyllithium and *m*-diisopropenylbenzene below the ceiling temperature and without any catalyst, which inevitably results in a mixture of the compounds with various functionalities. Yan and Zhou[12] have developed a kinetic theory for the reaction of living polymers with divinyl compounds, which is also amenable to the reaction between sec-butyllithium and *m*-diisopropenylbenzene with an arbitrary molar ratio. In the case of equivalent quantities of sec-butyllithium and *m*-diisopropenylbenzene being added to the reaction system, the derivation of the molecular weight distribution function, the number- and the weight-average molecular weights, the number- and the weight-distributions of functionality, and the average functionality of the resulting adducts are sketched below.

Let $P_{l,m}$ represent both the adduct with l residual sec-butyllithium groups and m *m*-diisopropenylbenzene units, and its concentration. If the intramolecular ring formation is negligible[13], we can find from the structural formula of the adduct that there are $m - l + 1$ residual double bonds in $P_{l,m}$. Therefore, the kinetic differential equation appropriate for the reaction under consideration reads:

$$\begin{aligned}\frac{\mathrm{d}P_{l,m}}{\mathrm{d}t} = \frac{k}{2} \sum_{\substack{0\le i\le m \\ j\le \min(l,i+1)}} &\{(i-j+1)P_{j,i}(l-j)P_{l-j,m-i} \\ &+ jP_{j,i}(m-i-l+j+1)P_{l-j,m-i}\} \\ &- k(m-l+1)P_{l,m} \sum_{\substack{i\ge 0 \\ j\le i+1}} jP_{j,i}\end{aligned}$$

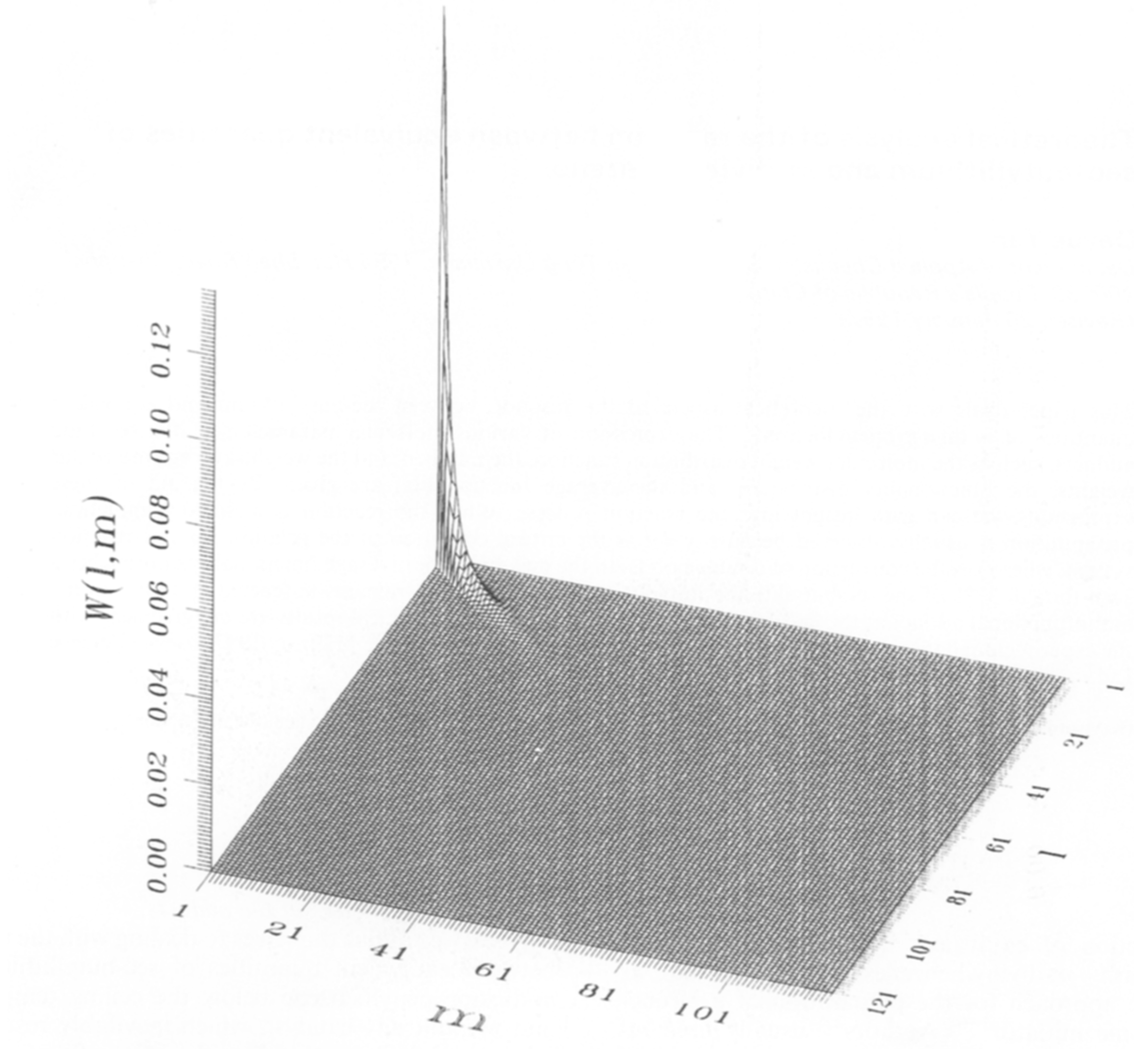

Figure 1 Molecular weight distribution: $x = 0.80$; $W(1,0) = 0.201$; $W(0,1) = 0.221$

$$-klP_{l,m}\sum_{\substack{i\geq 0\\ j\leq i+1}}(i-j+1)P_{j,i}, \quad m\geq 0, l\geq 0 \qquad (1)$$

In equation (1), the first summation is related to the formation of $P_{l,m}$, and other terms are connected with the disappearance of the adduct. Obviously $P_{1,0}$ and $P_{0,1}$ denote the concentrations of sec-butyllithium and *m*-diisopropenylbenzene, respectively. The initial conditions of equation (1) are: $P_{1,0}|_{t=0} = L$, $P_{0,1}|_{t=0} = L/2$ and $P_{l,m}|_{t=0} = 0, l \neq 0, m \neq 0$, where L symbolizes the initial concentration of sec-butyllithium. From the material balance conditions we have

$$\sum_{\substack{m\\ l\leq m+1}} lP_{l,m} = L \qquad (2)$$

and

$$\sum_{\substack{m\\ l\leq m+1}} mP_{l,m} = L/2 \qquad (3)$$

Now we define x as the conversion of double bonds of *m*-diisopropenylbenzene:

$$x = \frac{L - \sum_{m,l}(m-l+1)P_{l,m}}{L} = \frac{3}{2} - \sum_{m,l} P_{l,m}/L \qquad (4)$$

where $\sum_{m,l}(m-l+1)P_{l,m}$ is the concentration of residual double bonds in the reaction system. Equation (4) results in

$$\sum_{m,l} P_{l,m} = L(\tfrac{3}{2} - x) \qquad (5)$$

From equation (5) we further have

$$\frac{\mathrm{d}\sum_{m,l} P_{l,m}}{\mathrm{d}t} = -L\frac{\mathrm{d}x}{\mathrm{d}t} \qquad (6)$$

On the other hand, summing up both sides of equation (1), respectively, over indices l and m leads to

$$\frac{\mathrm{d}\sum_{m,l} P_{l,m}}{\mathrm{d}t} = -kL\sum_{i,j}(i-j+1)P_{j,i} = -kL^2(1-x) \qquad (7)$$

Comparing equation (6) with equation (7) we gain

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kL(1-x) \qquad (8)$$

Both sides of equation (1) are divided by the respective sides of equation (8); consequently a linear differential

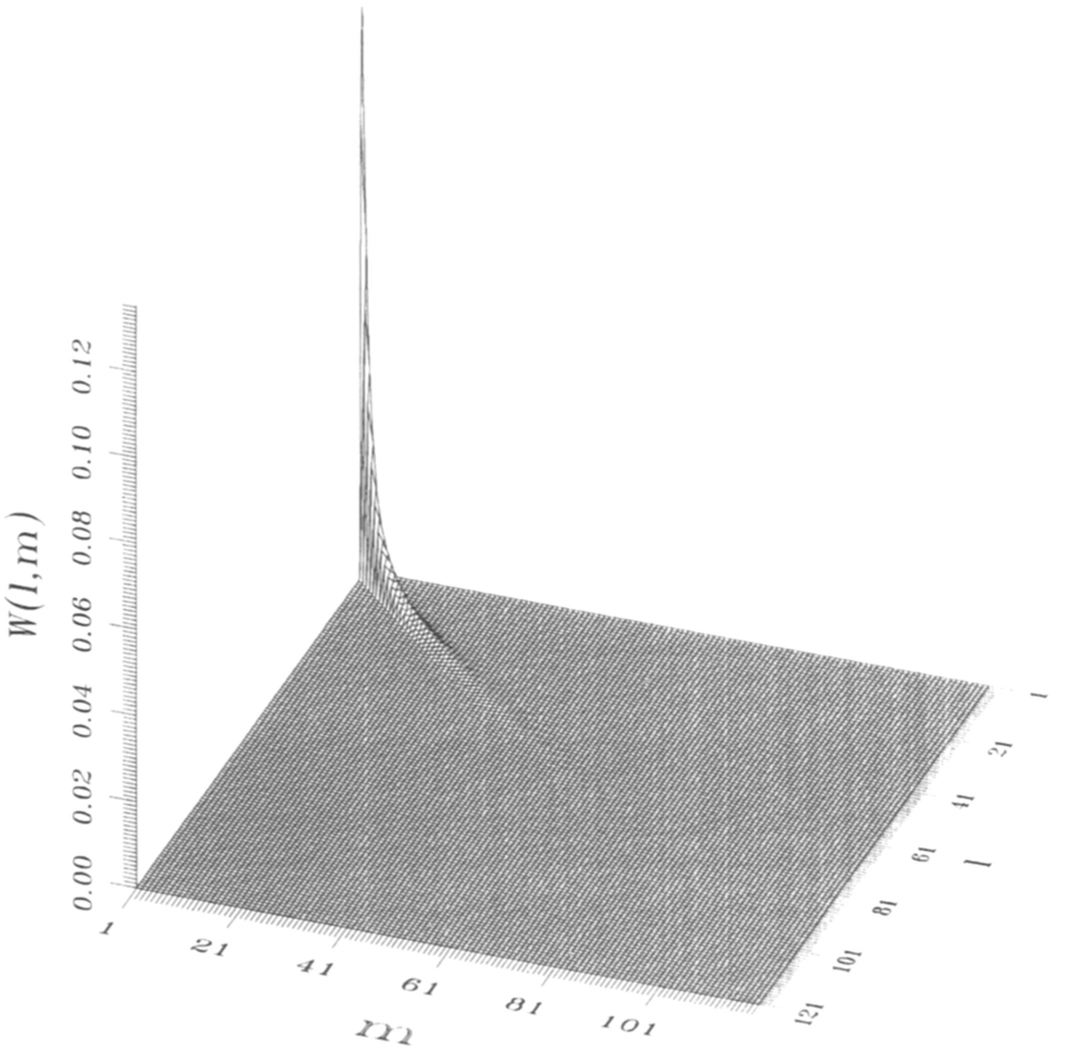

Figure 2 Molecular weight distribution: $x = 0.90$; $W(1,0) = 0.182$; $W(0,1) = 0.006$

equation is given:

$$\frac{dP_{l,m}}{dx} = \frac{1}{2L(1-x)} \sum_{\substack{0\le i\le m\\ j\le \min(l,i+1)}} \{(i-j+1)P_{j,i}(l-j)P_{l-j,m-i} + jP_{j,i}(m-i-l+j+1)P_{l-j,m-i}\} - (m-l+1)P_{l,m}/(1-x) - lP_{l,m} \quad (9)$$

The initial condition should be changed accordingly. Finally, we obtain the analytical solution of equation (9) by induction:

$$P_{l,m} = \frac{Ll^{m-1}}{(m-l+1)!l!} x^{l+m-1}(1-x)^{m-l+1} e^{-lx} \quad (10)$$

Furthermore, we can derive various moments of the molecular weight distribution of the adducts in terms of equation (10) and then obtain the expressions of number- and weight-average molecular weights, number- and weight-distribution of functionality, as well as the average functionality:

$$\overline{M_n} = \frac{\sum_{m,l}(lw_1 + mw_2)P_{l,m}}{\sum_{m,l} P_{l,m}} = \frac{2w_1 + w_2}{3 - 2x} \quad (11)$$

$$\overline{M_w} = \frac{\sum_{m,l}(lw_1 + mw_2)^2 P_{l,m}}{\sum_{m,l}(lw_1 + mw_2)P_{l,m}} = \frac{2(w_1 + xw_2)^2 + (1 - x^2)w_2^2}{(1 - x^2)(2w_1 + w_2)} \quad (12)$$

$$P_l = \sum_m P_{l,m} = L\frac{x^2(lx^2)^{l-2}}{l!} e^{-lx^2} \quad (13)$$

$$P_{l,w} = \frac{lP_l}{\sum_l lP_l} = \frac{(lx^2)^{l-1} e^{-lx^2}}{l!} \quad (14)$$

and

$$\overline{P_l} = \frac{\sum_l lP_l}{\sum_l P_l} = \frac{2}{2 - x^2} \quad (15)$$

where w_1 and w_2 are the molecular weights of sec-butyllithium and *m*-diisopropenylbenzene, respectively. In equation (13), we have summarized $P_{l,m}$ over index m; hence, the concentration of *m*-diisopropenylbenzene is not involved in the number- and weight-distributions of

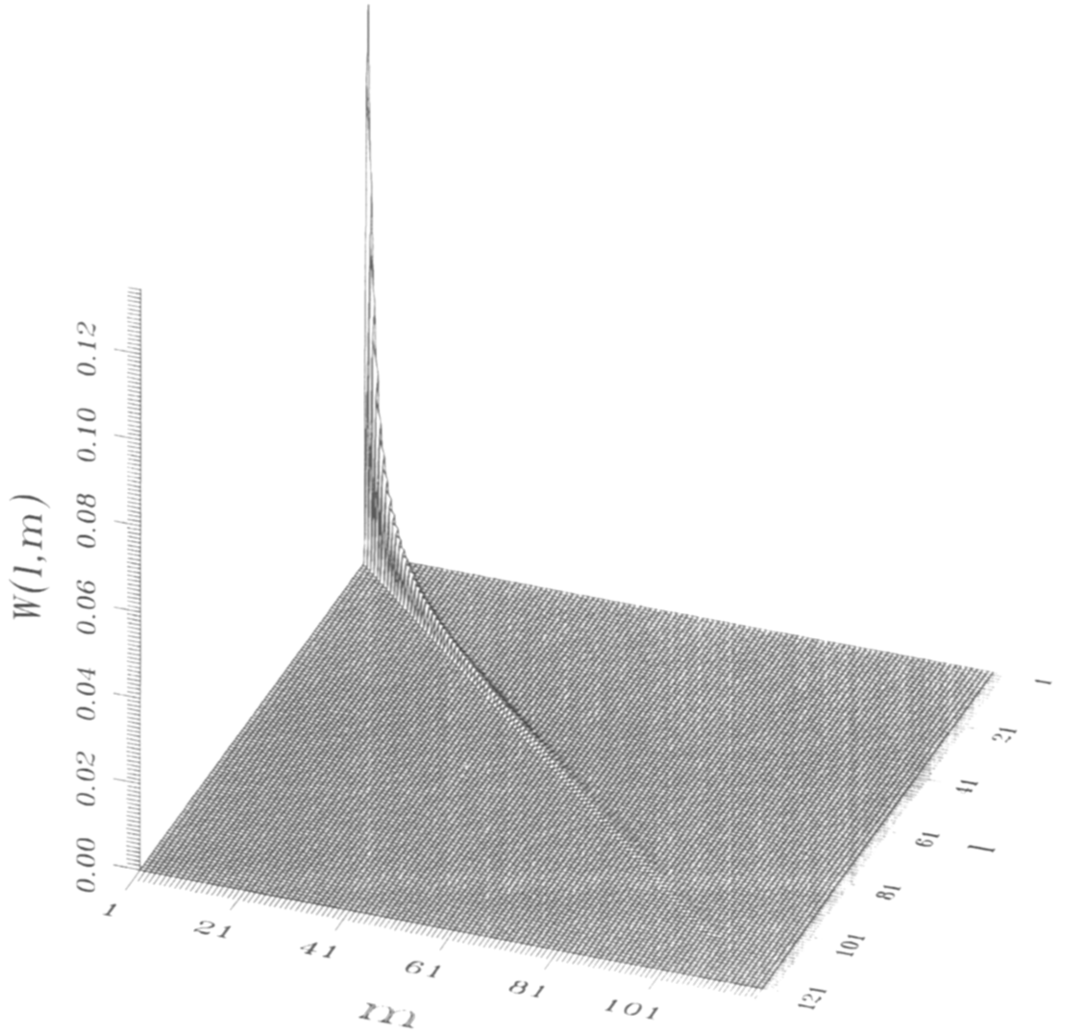

Figure 3 Molecular weight distribution: $x = 0.99$; $W(1,0) = 0.116$; $W(0,1) = 0$

functionality or the average functionality. In accordance with equations (10)–(15), we can predict the molecular parameters of the resulting adducts and try to explain the experimental phenomena aforementioned.

Numerical results and discussion

The normalized molecular weight distribution is defined by

$$W(l,m) = \frac{(lw_1 + mw_2)P_{l,m}}{L(w_1 + w_2/2)} \qquad (16)$$

where $w_1 = 64$ and $w_2 = 158$. The plots of molecular weight distribution at $x = 0.8$, 0.9 and 0.99 are shown in *Figures 1–3*, respectively. For the convenience of drawing, the figures start from $l = 1$ and $m = 1$, and the values of $W(1,0)$ and $W(0,1)$ are given in the legends of *Figures 1–3*, respectively. When the conversion reaches 0.99, the peak of molecular weight distribution is located at $l = 2$ and $m = 1$, and the distribution plot has such a long tail that 8.76% adducts by weight- are beyond *Figure 3*. The number- and the weight-average molecular weights varying with the conversion of double bonds are illustrated in *Figure 4*. One finds from *Figure 4* that the weight-average molecular weight approaches infinity while the conversion of double bonds reaches 1. It means that for the reaction system, $x = 1$ is the critical condition of gelation. This is why precipitation takes place when the reaction is close to completion. *Figure 5* demonstrates the relationship between the average functionality and the conversion of double bonds. The average functionality of the final adducts at $x = 1$ is exactly equal to 2, even though there are various adducts with different functionalities in the reaction system. *Figure 6* is the plot of the weight distribution of functionality *versus* the conversion of double bonds. The weight distribution of functionality at $x = 1$ is elucidated in *Figure 7*. The numerical calculation shows that 37% sec-butyllithium molecules initially added to the reaction system remain unreacted and join to the monofunctional adducts when the reaction approaches to completion. In general, the theoretical conclusions of this paper coincide with those of the experimental investigation reported by Cameron and Buchan[9]. The addition of sec-butyllithium to equivalent quantities of *m*-diisopropenylbenzene in the absence of catalyst and below the ceiling temperature inevitably gives rise to a mixture of bi- and poly-functional materials, together with monofunctional species.

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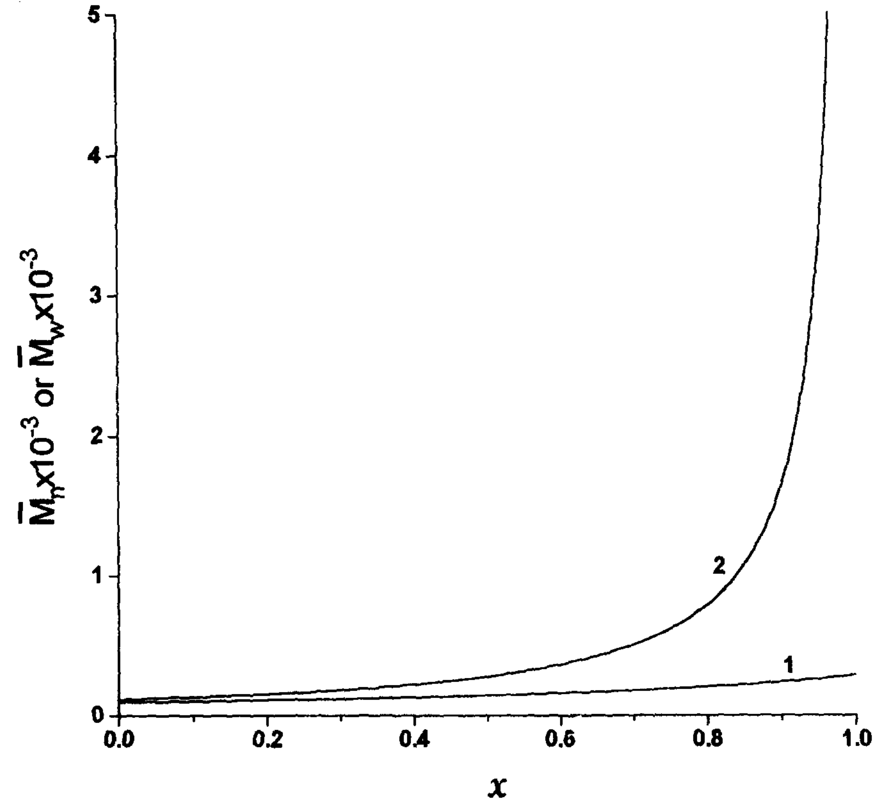

Figure 4 Relationships between the number- and the weight-average molecular weights and the conversion of double bonds: (1) $\bar{M}_n$; (2) $\bar{M}_w$

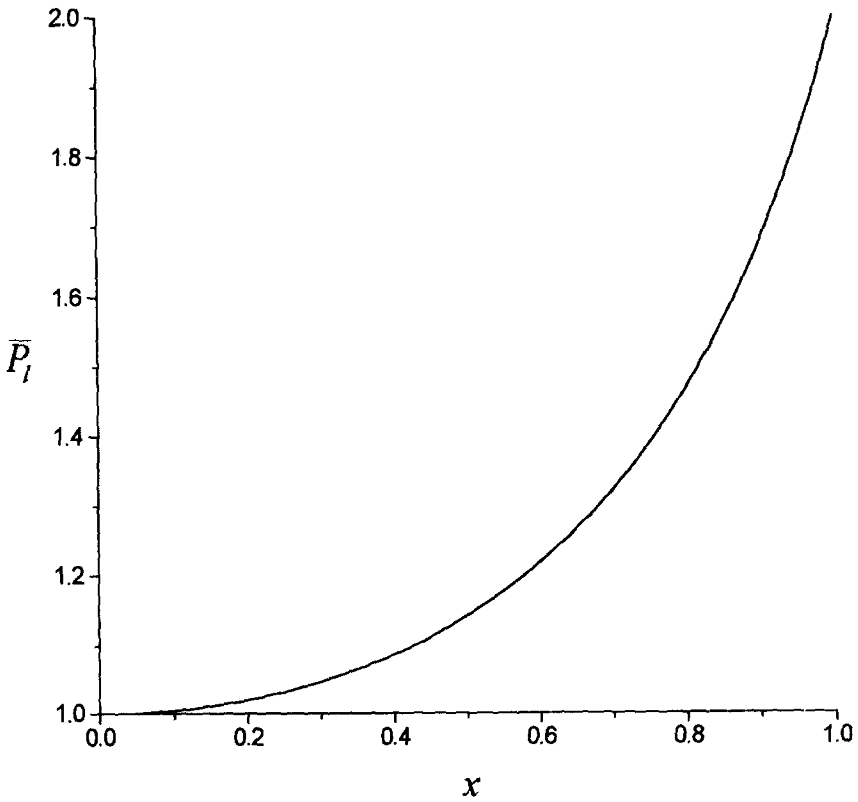

Figure 5 Plot of the average functionality *versus* the conversion of double bonds

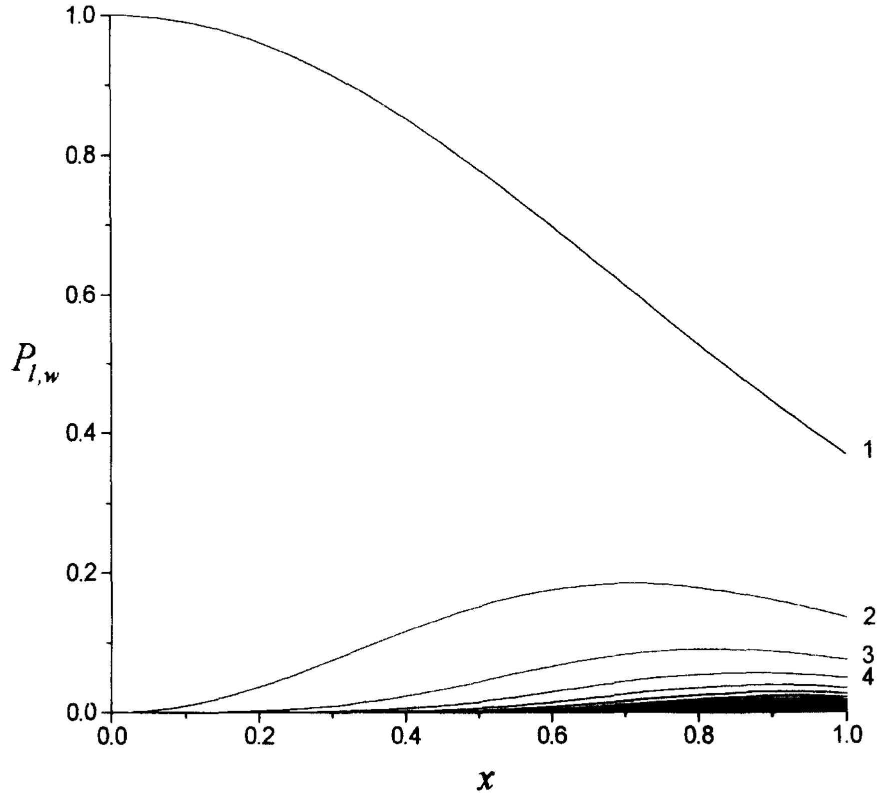

Figure 6 Weight-distribution of functionality varying with the conversion of double bonds: (1) $l = 1$; (2) $l = 2$; (3) $l = 3$; (4) $l = 4$, etc.

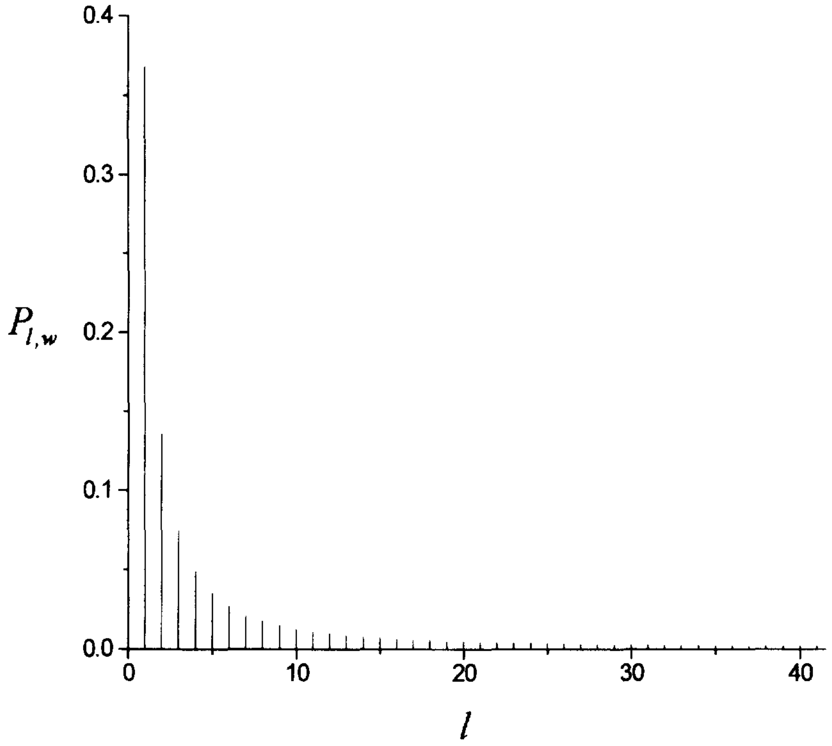

Figure 7 Weight distribution of functionality when $x = 1$

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