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(41) The rate constant for $^3\Sigma_g^-O_2$ quenching of $^1\Delta_gO_2$ in the gas phase is $\sim 1.9 \pm 0.5 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}.[42] Transformation to solution phase units yields 1.1×10^3 s^{-1} M^{-1}. In a series of solution-phase experiments, we have obtained evidence which suggests that 1.1×10^3 s^{-1} M^{-1} is indeed a reasonable upper limit for the quenching rate constant. Specifically, first-order kinetics were obtained with *oxygen concentration independent* lifetimes when $^1\Delta_gO_2$ decay was monitored in both aerated ($[O_2] \simeq 1.3 \times 10^{-3}$ M) and oxygenated ($[O_2] \simeq 8 \times 10^{-3}$ M) solutions[16,43] of CD_3CN and C_6D_6. [$\tau_\Delta(CD_3CN) = 1.5 \pm 0.1$ ms and $\tau_\Delta(C_6D_6) = 770 \pm 30$ μs.] The rate constant for $^1\Delta_gO_2$ decay can be expressed as the sum of a pseudo-first-order solvent-dependent term[18] and an $^3\Sigma_g^-O_2$ quenching term ($\tau_\Delta^{-1} = k_0 + k_q[^3\Sigma_g^-O_2]$). At these oxygen concentrations, our results indicate that the product $k_q[^3\Sigma_g^-O_2]$ is is still too small to influence k_0 when $k_0 \simeq (1.5\ \text{ms})^{-1}$. Recent results of Schmidt and Brauer[12] indicate that k_q may, in fact, be substantially smaller than 1.1×10^3 s^{-1} M^{-1}. In their study, $^1\Delta_gO_2$ decay in CS_2 ($\tau_\Delta \simeq 34$ ms) was found to be oxygen concentration independent. In solvents where $\tau_\Delta \geq 500$ μs, τ_Δ is often limited by other $^1\Delta_gO_2$ quenchers, e.g., the $^1\Delta_gO_2$ sensitizer itself or photolytically created species.[18] Our CD_3CN data were recorded at very low laser energy (0.7 mJ/pulse^{-1} at 355 nm), using a low sensitizer concentration (7×10^{-5} M phenazine). The τ_Δ obtained is larger than those previously reported[8] and, therefore, is likely a more accurate representation of intrinsic solvent-induced quenching in CD_3CN.
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A Lattice Model of the Isotropic Phase to Mesophase Transition of Polymers with Semiflexible Backbone and Flexible Side Chains

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ABSTRACT: The transition temperatures of semiflexible polymers with flexible side chains from an ordered (liquid crystalline) state to the disordered (isotropic) state are calculated based on a lattice model. In order to account for the flexibility of the backbone, a modification of the original approach by Flory is developed. The transition temperatures of a series of poly(3-*n*-alkyl-4-hydroxybenzoate)s are calculated by using this approach. The results agree well with experimental data.

Introduction

The statistical thermodynamics of solutions of stiff chain molecules has been the subject of many investigations.[1-4,16] Although different models were proposed, most of them led to the conclusion that the dominant factor controlling the transition from the isotropic to the liquid crystalline phase is entropical in nature and is determined by the sizes and shapes of the macromolecules.

One of the most used models is the lattice model.[5,6] Although often critically discussed,[20] it has survived because it is very helpful for the calculation of the configurational partition functions of molecules under the con-

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straint that overlaps have to be avoided. This model was also applied to semiflexible chains by Flory.[7] He introduced an expression for the temperature-dependent flexibility of the chain and investigated the phase transitions of binary mixtures of a polymer and a solvent.

Let z be the coordination number of the lattice (in this paper, we always work with a cubic lattice, i.e., $z = 6$). When a chain is introduced into the isotropic phase, f is the probability that the "bond" from the last lattice point occupied by the chain to the next does not go in the same direction as the preceding "bond". ϵ is the energy for which the "straightforward" bond is favored over the $z - 2$ possibilities to make a kink. The probability, p, that a lattice place is still vacant is always taken as

$$p = \text{number of all vacant lattice sites}/n_0$$

where n_0 is the number of all lattice sites. After all chains are introduced into the isotropic phase, the solvent is placed on all remaining lattice sites. The expression for the free energy is[7]

$$\Delta G_M = RT\{n_1 \ln v_1 + n_2 \ln v_2 + \chi x n_2 v_1 - n_2 \ln (xz/2) + n_2(x - 1) + n_2(x - 2)[f \ln f + (1 - f) \ln (1 - f) - f \ln (z - 2) + f\epsilon/kT]\} \quad (1)$$

where n_1 is the number of lattice sites occupied by a solvent, n_2 is the number of polymer molecules, x is the number of lattice sites occupied by one polymer molecule, $v_1 = n_1/n_0$, $v_2 = xn_2/n_0$, i.e., v_1 and v_2 are the volume fractions of the solvent and the polymer, and χ is the parameter governing the mixing free energy, arising from intermolecular contacts. k is the Boltzmann constant.

Since the free energy in the isotropic phase is supposed to be minimal with respect to f for every temperature, i.e, $\partial \Delta G_M / \partial f = 0$, we obtain[7]

$$f = (z - 2) \exp(-\epsilon/kT)\{1 + (z - 2) \exp(-\epsilon/kT)\}^{-1} \quad (2)$$

This model causes the so-called "entropy catastrophe" at very small values of f and high polymer concentrations; i.e., the number of all possible configurations will be less than 1. This does not make physical sense, because at least one configuration exists always. The reason for this effect is that eq 1 is derived for the disordered, isotropic state and the assumption for the probability of vacancies p is incorrect for ordered phases.[8] To avoid this catastrophe, Flory introduced an additional model for the ordered phase: he assumed a "quasi-crystalline lattice model", a system of parallel rods mixed with solvent molecules of the same diameter, which corresponds to an ideal binary mixture of particles in one dimension. This gives the following free energy:[7]

$$\Delta G_M' = RT\{n_1' \ln n_1' + n_2' \ln n_2' - (n_1' + n_2') \ln (n_1' + n_2') + \chi' x n_2' v_1'\} \quad (3)$$

The prime signifies the ordered phase. For $v_2 = 1$, we obtain $\Delta G_M' = 0$, and the disordered phase is stable only if $\Delta G_M < 0$; i.e.,[7]

$$f > 1 - \frac{1}{e}\left\{\frac{zx}{2e}\right\}^{1/(x-2)} \quad (4)$$

and for $x \rightarrow \infty$,[7]

$$f > 1 - 1/e \approx 0.63 \quad (5)$$

While in ref 7 the case of a binary system of a polymer and a solvent is treated, we are interested in a single-phase system of a semiflexible polymer with flexible side chains. Assuming that the side chains in the ordered (liquid crystalline) phase have their full flexibility when the phase transition point is reached, i.e., all possible configurations of the side chains are statistically adopted, we can treat them like a solvent, i.e., the main chain can move as free as in a solvent. Solid-state ^{13}C NMR measurements of poly(1,4-phenylene 2,5-bis(hexadecyloxy)terephthalate), for example, have shown that above 390 K, i.e., within the mesophase, the concentration of rigid all-trans side chains is reduced to zero.[19] ^2H NMR of the same polymer, deuterated in the center of the side chain, also shows that within the mesophase the side chains have liquidlike mobility.[18] From molecular dynamics calculations, we know how much of the side chain should be considered to belong to the main chain. The criterion for this is that all orientations relative to the main chain are possible.

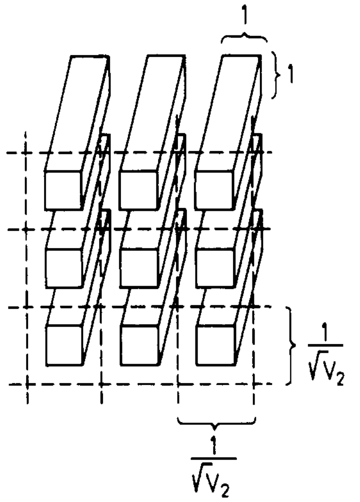


Figure 1. Arrangement of the main chains in the ordered phase: the average cross-sectional area available to a main chain is $1/v_2$.

In this single-phase system, it is obvious that $n_1 = n_1'$, $n_2 = n_2'$, $v_1 = v_1'$, and $v_2 = v_2'$. Like Flory,[7] we set $\chi = \chi'$. While in the case of pure main-chain liquid crystals the enthalpy of interaction plays a minor role compared with the entropy, the influence of the former is even smaller when the contact between the main chains is diminished by the completely flexible side chains at the phase transition point. Obviously, the phase transition now takes place when $\Delta G_M = \Delta G_M'$ and one can deduce from eq 1–3 the following condition for the transition from the ordered to the disordered (isotropic) phase:

$$f = 1 - \left\{\frac{z}{2}\right\}^{1/(x-2)} \exp\left\{-\frac{x-1}{x-2}\right\}\left\{\frac{x - xv_2 + v_2}{x}\right\}^{[-x+xv_2-v_2]/[v_2(x-2)]} \quad (6)$$

With $v_2 = 1$, eq 6 can be transformed to eq 4.

Equation 6 is derived under the assumption that in the ordered phase all main chains must be parallel. While this assumption seems reasonable for a stiff polymer without side chains, it is certainly wrong for a semiflexible polymer with flexible side chains. In this case, one has also to introduce a possible flexibility into the model for the liquid crystalline phase. The remaining part of this paper shall treat this topic.

Theory

The average cross-sectional area that is available to a main chain is $1/v_2$ if the edge of a lattice cube is unity. The edge of this area then is $1/v_2^{1/2}$ (see Figure 1). So a tube of the dimensions $1/v_2^{1/2}$, $1/v_2^{1/2}$, and x is available to every main chain.

If a main chain is bent one time in this tube, it will touch the next wall and has to be bent into the preferred direction again. As long as $v_2 > 0.25$, this must happen directly, and there is no possibility to bend perpendicular

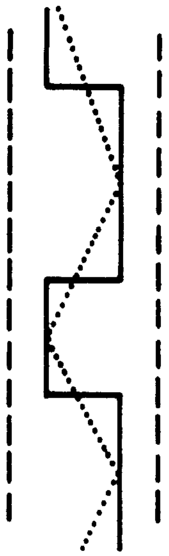


Figure 2. Projection of the path of the main chain in the "tube".

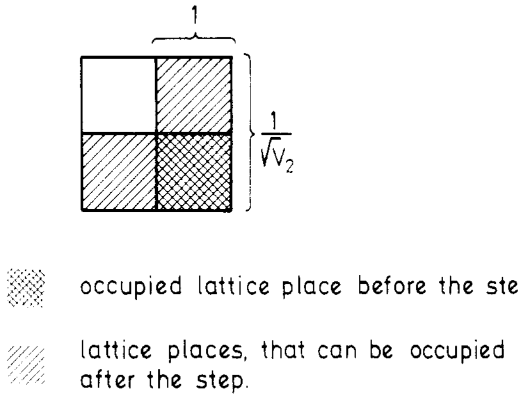


Figure 3. Cross section of a tube available to a main chain.

to the preferred direction again or to fold back because there is not enough space in the tube. This gives a step from two bends (see the drawn line in Figure 2). Such a step would have an energy of $\epsilon' = 2\epsilon$ higher than the straightforward conformation. As one can see from Figure 2, this assumption is very unrealistic because a real chain would follow the dotted path. One can therefore hope to fit real conditions better by setting $\epsilon' = \epsilon$.

After every step, the main chain has

$$\alpha = 2/v_2^{1/2} - 2 \tag{7}$$

possible lattice sites to be placed (see Figure 3). Even if the main chain is completely rigid, its direction does not have to be completely parallel to the tube, i.e., the order parameter can be less than 1. Without an additional energy, the end of the chain thus has $\alpha + 1$ possibilities to be placed.

Let f' be the probability of a step. Then one has $(x - 2)f'n_2$ steps in the model. They can be put in

$$\binom{(x-2)n_2}{(x-2)f'n_2}$$

different ways and open up $\alpha^{(x-2)f'n_2}$ possible conformations. The ends of the chains contribute a factor of $(\alpha + 1)^{n_2}$. Thus, the partition function is given by

$$Q_M' = \frac{(n_1 + n_2)!}{n_1!n_2!}\alpha^{(x-2)f'n_2}(\alpha + 1)^{n_2}\binom{(x-2)n_2}{(x-2)f'n_2} \times \exp\{-(x-2)f'n_2\epsilon'/kT - \chi'xn_2v_1\} \tag{8}$$

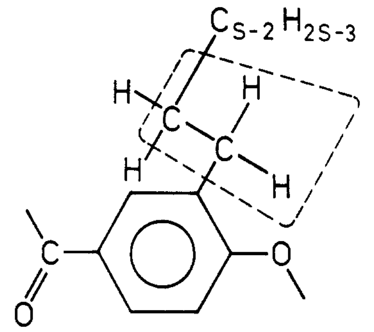


Figure 4. Repeat unit of a poly(3-*n*-alkyl-4-hydroxybenzoate): the marked part of the side chain is attributed to the main chain.

Calculating $\Delta G_M' = -RT \ln Q_M'$ using Stirling's approximation yields

$$\Delta G_M' = -RT\{(n_1 + n_2) \ln (n_1 + n_2) - n_1 \ln n_1 - n_2 \ln n_2 + (x-2)f'n_2 \ln \alpha + n_2 \ln (\alpha + 1) - (x-2)f'n_2 \ln f' - (x-2)(1-f')n_2 \ln (1-f') - (x-2)f'n_2\epsilon'/kT - \chi'xn_2v_1\} \tag{9}$$

Minimizing the free energy of the ordered phase with respect to f', i.e., setting $\partial\Delta G_M'/\partial f' = 0$, one obtains

$$f' = \alpha \exp(-\epsilon'/kT)\{1 + \alpha \exp(-\epsilon'/kT)\}^{-1} \tag{10}$$

analogous to eq 2. The phase transition point now is characterized by $\Delta G_M = \Delta G_M'$, which is equivalent to $F(f,f') = 0$ with

$$F(f,f') = \left\{1 + x\left(\frac{1}{v_2} - 1\right)\right\} \ln \left\{1 - \frac{v_2}{x}(x-1)\right\} + \ln (\alpha + 1) - (x-2) \ln (1-f') + (x-2) \ln (1-f) - \ln \left(\frac{z}{2}\right) + x - 1 \tag{11}$$

Equation 11 is deduced from eq 1, 2, 9, and 10. $\chi = \chi'$ is assumed.

Application of the Model to a Real Polymer

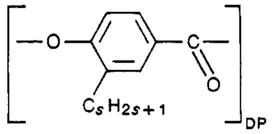
We apply this model to the poly(3-*n*-alkyl-4-hydroxybenzoate)s[9] because this class of polymers meets the required conditions: they have a semiflexible main chain and flexible side chains. The intrinsic stiffness of the main chain was recently investigated by the method of molecular dynamics,[10] yielding a persistence length of 65 Å at 300 K. In each hydrocarbon side chain, the third bond next to the main chain can achieve every orientation relative to the main-chain direction. Therefore, 1.5 methylene groups are attributed to the main chain (see Figure 4). The relative volume of the main-chain v_2 is calculated knowing the density of the pure main-chain material and the densities of pure hydrocarbons.[12] For the main-chain material, i.e., poly(4-hydroxybenzoate), the density of the high-temperature phase (1.32 g/cm^3) is used.[11] From the densities of the hydrocarbons, one can calculate the volumes of the methylene and the methyl groups. Taking into account that the length of a monomer unit is 6.2 Å,[10] the edge of a lattice cube, i.e., the average diameter of the chain, is 5.54 Å. The latter is calculated via

$$d = [(\text{volume of a repeat unit including 1.5 methylene groups})/(\text{length of a repeat unit})]^{1/2} \tag{12}$$

(see also ref 21).

The number of lattice cubes filled by one main chain is now $x = (6.2/5.54)\text{DP}$.

Table I
Temperatures of the Liquid Crystalline to Isotropic Phase Transition ($T_{lc,i}$) of Polymers of the General Structure



		exptl obsd transition temp, $T_{lc,i}$,[d] °C			calcd temp and flexibilities at the transition point						
					method 1	method 2			method 3		
s[a]	DP[b]	not annealed	annealed	v_2[c]	$T_{lc,i}$, °C	T_{lci}, °C	f	f'	$T_{lc,i}$, °C	f	f'
5	40	320	345[e]	0.61	273	288	0.32	0.008	348	0.37	0.08
6	37	261	272[f]	0.56	238	254	0.29	0.007	318	0.35	0.08
10	17	227	230[g]	0.43	129	166	0.21	0.005	238	0.28	0.09
12	84		225[h]	0.38	146	157	0.20	0.005	243	0.28	0.11
14	27	212		0.34	104	133	0.17	0.004	223	0.26	0.11
16	40	208		0.31	99	121	0.16	0.004	219	0.26	0.12
16	30	201		0.31	92	119	0.16	0.004	217	0.26	0.12
16	23	202		0.31	82	118	0.16	0.003	215	0.26	0.12
18	35	202	206[i]	0.29	82	108	0.15	0.003	215	0.26	0.13

[a] s = number of carbon atoms of the *n*-alkyl side chains. [b] DP = degree of polymerization. [c] v_2 = volume fraction of the main chain. [d] The given values are taken from the maxima of the DSC curves. [e] Annealing conditions: 13 h at 230 °C. [f] Annealing conditions: 18 h at 230 °C. [g] Annealing conditions: 20 h at 200 °C. [h] Annealing conditions: 18 h at 200 °C. [i] Annealing conditions: 19 h at 170 °C.

Table II
Temperatures of the Liquid Crystalline to Isotropic Phase Transition ($T_{lc,i}$) of Oligomers with a Propyl Side Chain ($v_2 = 0.74$)

		calcd temp and flexibilities at the transition point						
		method 1	method 2			method 3		
DP[a]	$T_{lc,i}$, °C (measd)	$T_{lc,i}$, °C	$T_{lc,i}$, °C	f	f'	$T_{lc,i}$, °C	f	f'
7	247	230	272	0.31	0.004	301	0.33	0.04
6	221	195	244	0.28	0.003	270	0.31	0.03
5	191	140	203	0.25	0.002	224	0.26	0.03
4	156	28	130	0.17	0.001	144	0.19	0.02

[a] DP = degree of polymerization.

From a persistence length of $a = 65$ Å and a bond length of $l = 5.54$ Å, the characteristic ratio $c_\infty = 2a/l - 1 = 22.47$ is calculated.[13] Via[13]

$$c_\infty = (1 + \langle\cos\vartheta\rangle)/(1 - \langle\cos\vartheta\rangle) \qquad (13)$$

$\langle\cos\vartheta\rangle = 0.9148$ is obtained; $\langle\cos\vartheta\rangle$ is the average cosine of the complement of the bond angle in a freely rotating chain. The harmonic approximation

$$\langle\cos\vartheta\rangle \approx \cos\langle\vartheta\rangle(1 - \tfrac{1}{2}\langle\Delta^2\vartheta\rangle) \qquad (14)$$

gives us, with the average complement of the bond angle $\langle\vartheta\rangle = 0$, the standard deviation of ϑ

$$\Delta\vartheta = (\langle\Delta^2\vartheta\rangle)^{1/2} = 23.65°$$

If there are only two possibilities—the straightforward conformation and a 90° bend—the probability of the latter is given by $f = (23.65°)^2/(90°)^2 = 0.06905$ at 300 K.

With eq 2, $-\epsilon/k = -1196$ K is obtained. Now all information is accumulated to apply the models. We use three methods:

(1) The temperature for the transition of the liquid crystalline to the isotropic phase is calculated via eq 6 and 2.

(2) For a given temperature, f and f' are calculated by eq 2 and 10, using $\epsilon' = 2\epsilon$. The results are inserted into eq 11. Varying the temperature, the zero transition of $F(f,f')$ is searched, which gives us the phase transition point.

(3) This method is the same as the previous, but we set $\epsilon' = \epsilon$.

It can be shown that in the limit of $v_2 \to 1$ the three methods give the same results as one receives by application of eq 4 and 2; i.e., for pure main chains, the limiting behavior of the models is consistent with the original model of Flory.[7]

Results and Discussion

The temperatures of transition of the poly(3-*n*-alkyl-4-hydroxybenzoate)s from a liquid crystalline phase to the isotropic phase as given in Tables I and II for annealed and nonannealed samples have been measured by differential scanning calorimetry and hot-stage polarizing microscopy. The degree of polymerization of the polymers was determined by ^{1}H NMR end-group analysis. The purity of the oligomers was checked by IR, NMR, HPLC, and elemental analysis.[17]

As one can see from Tables I and II, method 1, which does not take into account flexibility of the backbone in the liquid crystalline phase, gives phase transition temperatures much below the experimentally determined values. The difference between experimental and calculated values increases with the length of the side chain. Method 2 gives higher transition temperatures because the additional degrees of freedom provided by the allowed flexibility favor the ordered phase. But for longer side chains, the difference between calculated values and the measurements is still too large. The reason is the overestimation of the energy, needed for a "step" in the ordered phase. This is easy to see considering the decreasing values of f' with increasing length of the side chain. With $\epsilon' = \epsilon$, method 3 gives us phase transition temperatures that are in good agreement with experiment. Method 2 even fits the phase transitions of the oligomers (see Table II) slightly better than method 3. This is due to the short length of the side chains that obviously can no longer be treated as a continuous liquid in which the main chain moves freely.

We can draw the conclusion that the model of a semiflexible main chain in a "liquid" of flexible side chains gives us the best description of the liquid crystalline phase near the transition to the isotropic phase.

The following conditions must be fulfilled to calculate phase transition points with this model:

(1) The intrinsic stiffness of the main chain must be known. For example, if the value of the persistence length is doubled, our calculations give results of about 100 °C above the experimental values.

(2) Near the transition from the liquid crystalline phase to the isotropic phase, the side chains must have reached liquidlike mobility; i.e., they must be able to achieve every orientation relative to the main chain, giving α possibilities for the main chain to be placed after every step (see eq 7).

(3) Clusters of two or more main chains near the transition point do not exist.

(4) $v_2 > 0.25$ must be fulfilled; i.e., the relative volume of the side chains is not too large.

There are still some sources of ambiguity in the model: In the case of short side chains, the extent to which they are attributed to the main chain is important. For longer side chains ($v_2 \leq 0.5$), this factor has only a very small influence. The model is based on pure entropic effects, and thus enthalpic effects due to specific interactions between different chains are not taken into account. Recent results support this approximation: Auriemma et al.[21] found, for nematic dimers constituted of two rigid groups linked by flexible spacers, that the isotropization temperatures, calculated in a lattice model, coincide with the experimental values, when the orientation-dependent interactions equal zero. Furthermore, the temperature dependence of v_2 and effects caused by polydispersity are neglected. The latter problem is less relevant for higher degrees of polymerization because for $x \rightarrow \infty$ the phase transition temperature approaches a limiting value.

Krigbaum[14] proposed to treat semiflexible polymers in the same way as stiff polymers, referring to Flory.[15] He took the flexibility of the chain into account by using the Kuhn length instead of the real contour length. In the model that we propose here, this idea is refined by calculating two different flexibilities, one for the isotropic phase and one for the liquid crystalline phase.

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Registry No. 4-Hydroxy-3-pentylbenzoic acid (homopolymer), 120411-51-0; 4-hydroxy-3-pentylbenzoic acid (SRU), 120411-52-1; 4-hydroxy-3-hexylbenzoic acid (homopolymer), 119865-15-5; 4-hydroxy-3-hexylbenzoic acid (SRU), 119865-56-4; 4-hydroxy-3-decylbenzoic acid (homopolymer), 119865-17-7; 4-hydroxy-3-decylbenzoic acid (SRU), 119865-57-5; 4-hydroxy-3-dodecylbenzoic acid (homopolymer), 119865-19-9; 4-hydroxy-3-dodecylbenzoic acid (SRU), 119865-58-6; 4-hydroxy-3-tetradecylbenzoic acid (homopolymer), 119865-21-3; 4-hydroxy-3-tetradecylbenzoic acid (SRU), 119865-59-7; 4-hydroxy-3-hexadecylbenzoic acid (homopolymer), 119865-23-5; 4-hydroxy-3-hexadecylbenzoic acid (SRU), 119865-60-0; 4-hydroxy-3-octadecylbenzoic acid (homopolymer), 119865-25-7; 4-hydroxy-3-octadecylbenzoic acid (SRU), 119865-61-1.

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