A nano-second scale in situ probe reveals that a bulk linear polymer undergoes a sharp phase transition as a function of the degree of conversion, as it nears the glass transition. The scaling behaviour is in the same universality class as percolation. The exponents $\gamma$ and $\beta$ are found to be $1.7 \pm 0.1$ and $0.41 \pm 0.01$ in agreement with the best percolation results in three dimensions.

PACS numbers: 64.60.Ak, 64.70.P, 82.35.-x, 83.80.Sg

I. INTRODUCTION

Polymeric melts, or linear polymers in the bulk, exhibit a rich array of different behaviours, as a function of the temperature, specific volume (per chain), chain length (molecular weight), and timescale of observation, generally without sharp boundaries between the different regimes. Linear polymers in the bulk range from solid, glassy or leathery materials at low temperatures to rubbery, and eventually viscous fluids at higher temperatures or polymer to solvent volume ratios. The viscosity of bulk linear polymers typically increases with increasing chain length and/or degree of conversion as polymerization proceeds, and diverges near the glass transition. The glass transition temperature is a function of the average chain length, for small to moderate length chains, but ceases to depend on the molecular weight for relatively long chains. The rheological or viscoelastic properties can thus be studied experimentally either as a function of the temperature, or as a function of the reaction time during the conversion process, as we have done here.

In this paper we would like to report that the extremely short-time response of bulk linear polymers probed by a fluorescent aromatic molecule displays a sharp transition as a function of the reaction time, which is a (nonlinear) measure of the degree of conversion. Immediately after the transition point, the melt is found to be glassy or rubbery for temperatures respectively below and above the glass transition temperature quoted for commercially available bulk PMMA, namely 106°C.

We find that this transition is characterised by percolation critical exponents. In an unpublished paper, we interpreted, erroneously, the percolation exponents found here as signalling the onset of the entanglement percolation transition. We now believe, for reasons to be discussed in this paper, that the fluorescence signal cannot, in fact, detect the formation of entanglement clusters.

In order to understand the physical nature of the processes underlying this percolation transition, one must follow the reaction kinetics, compare results with experiments directly measuring rheological properties in the course of the polymerization reaction, and also critically examine the steady state fluorescence technique employed. The “rheo-kinetics” of bulk polymerization is an extremely active and growing field of research, where different considerations based on free-volume, entanglement (or reptation), gel-effect and vitrification compete with and complement each other. We will interpret our results in the light of recent developments in the theory of the glass transition.

In section 2, we outline our experimental method, in section 3 we discuss the various mechanisms which come into play as the reaction proceeds. In section 4, we analyze the results in terms of percolation theory and extract the scaling exponents. In section 5, we present a discussion of the results.

II. THE EXPERIMENT

Our experimental method, the in situ monitoring of free-radical polymerization by a steady state fluorescence technique, is the same as the one we used to determine the critical exponents for the gel fraction ($\beta$) and the average cluster size ($\gamma$) in a previous paper, where we also found percolation exponents.

Fluorescence measurements yield direct, in situ information regarding the connectivity and available free volume in polymer melts and gels. The use of fluorescent probes to study the different environments in which the probe molecule finds itself, including experiments on polymerization, chemical gel formation, swelling and slow release of large molecules is an extremely well established method. Such measurements have also been applied to the study of glass formation, especially by the group of Ediger.

A. Experimental procedure

Pyrene was used as the fluorescence probe to detect the free-radical polymerization process of poly(methymethacrylate) (PMMA), a linear polymer. The characteristic time for the direct relaxation by fluorescent emission of the pyrene molecules is $\sim 10^{-9}$ seconds, a time scale much smaller than those involved in reptation, and of about the same order as Rouse dynamics. Thus, extremely fast “snap-
shots” of the effective network can be obtained as the polymerization reaction proceeds, without mechanically disturbing it, as one would have to do with conventional viscosity measurements.

Our experimental setup is the same as in ref. [11], except for the absence of a crosslinker, so that only linear polymers are obtained. The free radical polymerization of MMA was performed in the bulk in the presence of 2,2’-azobisisobutyronitrile (AIBN) as an initiator, at 60°, 70°, 75°, 85° and 125° C. The glass transition temperature of bulk PMMA is 105°C for the average chain lengths attained here. The pyrene molecule was excited at 345 nm and the variation in the fluorescence emission intensity, I, was monitored with the time-drive mode of the spectrometer, with a frequency of up to 10 points per second, staying at the 395 nm peak of the pyrene emission spectrum.

B. Results

In Fig. 1, we present our results for the normalized pyrene fluorescence intensities as a function of the reaction times, for different temperatures. The results for 125°C are very similar; however due to the much greater mobility and hence higher reaction rates at the higher temperature, the transition occurs already at 300 seconds, and therefore is off-scale in this figure.

The end product is rubbery at 125°C and glassy otherwise. In any case, at the end of the polymerization reaction the bulk polymer does not flow, but retains its

shape. The addition of solvent causes the polymer to swell, as a gel would, up to volume ratios of around 1 : 1. This indicates that the sample has definitely undergone a transition to a gel phase, due to the physical entanglements of the linear chains. Larger quantities of solvent dissolves the top layers, until, at a polymer to solvent ratio of about 1 : 2.5 ± 0.2 the whole sample becomes liquid. Since we started off with a bulk polymer, this ratio corresponds to the volume ratio at which the chains disentangle. This is in the same ballpark although a bit bigger than the conversion estimated from the value of I at the inflection point in Fig. 1, from $p_e \equiv I_e/I_{max} \approx 0.3$ (see [27]) and the percolation threshold for a cubic lattice in three dimensions ($p_c = 0.31$) [13]. For a cubic lattice, Kantor and Hassold [28] find an “entanglement threshold” very close to the ordinary percolation threshold, $p_e \approx p_c - 2 \times 10^{-7}$. (Also see [29, 30, 31]. It should be noted, however, that these authors consider clusters including branch points as well as those that cannot be pulled apart because of topological constraints.)

These considerations seem to point in the direction of a gelation (entanglement) transition at the onset of the sharp rise, ending, however, in a glassy phase, within a very small portion (duration wise) of the whole polymerization process. The glass transition temperature is swept up as the polymerization proceeds, until it crosses the temperature of the sample. [35] Even in the case of the run with the temperature held at 125°C, one is within about 20 degrees of the glass transition temperature, and one has to take into account the precursor effects that may be present. Qualitatively very similar behaviour observed many tens of degrees above the glass transition temperature [13], remains, however, a puzzle.

III. REACTION KINETICS AND RHEOLOGY

A close examination of the reaction kinetics of the free-radical polymerization process [35, 36, 37, 38, 39] reveals that in the initial stages (the flat, vanishingly small parts in Fig.1, preceding the rapid rise) the release of the free-radical which initiates chain formation, and the self- or cross-termination of the chains, balance each other out. Thus the chains which are formed are all more or less of the same length; i.e., as conversion proceeds at a fairly constant rate, the lengths of the chains that are formed are not growing on the average. As more of the monomers are converted, we reach a point where the fluorescence intensity starts picking up. This coincides with the rise in viscosity of the medium, with a concomitant rise in the rate of reaction, with the trapping of the free radicals [39, 40, 41], termed the “gel effect.” (Some authors refer only to the point where the reaction rate reaches a maximum, as the “gel effect” [39]). Somewhat counterintuitively, the reaction rate grows as the reaction becomes diffusion limited, because end to end- or self-termination of the chains become increasingly rare and the length of the growing chains can become very
large as a result. We will argue in this section that the fluorescent signal grows because of the trapping of the pyrene probes as well as the free radicals, in regions of relatively high density of the polymeric chains, where the cage effect comes into play.\[21, 51, 52, 53, 54, 55\]

The curves in Fig. 1 are quite typical of polymerization reactions with or without crosslinkers, and display a very sharp rise, with an inflection point, where the time derivative of the curve passes through a maximum, as shown in Fig. 2. (The duration and slope of the initial region of low conversion may depend on the temperature and weight fraction of the crosslinker or initiator.)

In an experiment involving a free-radical co-polymerization with cross linkers, Okay et al.\[39\] have monitored the viscosity of the medium using dilatometric techniques, and found that the gel point is located roughly at the onset of the gradual rise in the pyrene intensity curve, and definitely before the inflection point is reached. In the present experiment, since no crosslinkers are used, the increase in the viscosity may be ascribed to the physical entanglement of the polymer chains, giving rise to a purely geometrical gel phase (note that the unconverted monomers are easy to displace and provide the “sol” phase). The PMMA chains that are formed interact very weakly with each other, so that inter-chain attraction as in the formation of thermoreversible physical gels\[13, 14\] is less important here.

While chemical gelation in the presence of chemical cross-linkers exhibits a sharp transition which is modeled by percolation theory\[13, 14, 17, 18\], the formation of physical gels by bulk linear polymers is less well understood. It may be conjectured on the basis of scaling arguments and renormalization group calculations\[23, 49\] that this gel point is also controlled by percolation exponents, although it arises purely from entanglement effects and there are no (chemically bonded) branch points in the spanning network thus formed. Nevertheless, the above dilatometric findings on a similar system (albeit having crosslinkers) suggest that the pyrene fluorescence is probing the post-gel region and not the vicinity of the gel point. Further evidence for this is provided by a critical examination of the mechanism for the unquenching of the fluorescence itself.

The steady state fluorescence technique relies on the fact that the relaxation of excited aromatic molecules via indirect non-radiative transfer of energy to the high-frequency vibrational modes of the small solvent particles or monomers is forbidden\[51\] with the increased viscosity of the medium. The rates of intra-molecular or inter-molecular non-radiative transitions are determined by the availability of appropriately spaced levels either in the molecule itself or in the surrounding molecules. These levels are altered with the degree of conversion of the polymer melt, due to the local dynamical constraints arising from a reduction in the available free volume, and the consequent slowing down of segmental motions, leading to vitrification.\[22, 24, 25, 33, 34\] In this context, the consequent slowing down of segmental motions, leading from a reduction in the available free volume, and the consequent slowing down of segmental motions, leading to vitrification.\[22, 24, 25, 33, 34\] In this context,

free volume will mean the volume occupied by unconverted MMA molecules.

The connectivity may also contribute indirectly to retarding the local dynamics, in the present case through entanglement effects (since no chemical cross linkers are present). But the crossover between Rouse to reptation dynamics takes place above the glass transition (in temperature, or free volume). Moreover, it is generally believed that the cage effect\[3\] leading to this slowing down and vitrification occurs at much smaller spatial scales (in fact of the order of the polymeric bonds)\[56\] than those of Rouse or reptation\[2, 24, 25\] dynamics.

We can make a rough estimate of \(M_c\), the average length of the chains at the inflection point, from the value of the conversion fraction \(p_c \approx 0.3\)[27], assuming that the number of chains is approximately the same as the number of initiators. The molecular weights of the MMA and AIBN molecules are 100 and 164, respectively, and the experiments were performed with samples consisting of 1ml MMA (density 0.96 gr/ml) and 0.0026 gr AIBN. We find \(M_c \sim 180\), which is of the same order of magnitude as the chain length at which the chain dynamics crosses over from Rouse-like to reptation behaviour\[2, 24, 25\], as estimated by Kreer et al.\[26\] from simulations. This is an order of magnitude larger than an alternative estimate\[33, 41\] which can be obtained by comparing the average end to end distance to the diameter of the reptation “tube.”

On the other hand, the time scales involved in the cage effect are of the order of pico seconds, while in Rouse or reptation motion they range from nano to microsec-

![FIG. 2: The typical critical peak exhibited by the derivative of the fluorescence curve, at 75°C, in the vicinity of the critical point. The maximum is at \(t_{max}\), the half width at half maximum, \(t_{1/2}\), and the critical point, \(t_c\) are indicated.](image-url)
onds [22]. Therefore it would seem that those degrees of freedom which would be frozen out with respect to the pyrene probe with a time scale of the order of nanoseconds, would be the latter. Thus it is difficult to unequivocally identify the contributions to the unquenching of the pyrene fluorescence, as arising strictly from the connectivity (entanglements) or from the formation of density inhomogeneities that are the precursors of glass formation, merely from considerations of time and length scales.

Further information is provided by the ESR spectra in the course of the polymerization (free radical copolymerization of MMA and ethylene glycol dimethacrylate - EGDMA) [12]. These measurements reveal that the radical concentration exhibits a sharp peak right at the inflection point of the polymerizations curves, which are exactly similar to those appearing in Fig.1. Even more crucial is the fact that, in the region between the inflection point and where the curves flatten off, the ESR spectra switch from having 13 lines to 9 lines; with the 9 line spectra being contributed by radicals finding themselves in solid, i.e., glassy environments. [42, 45, 57]

A simulation [57] based on a random walk percolation model [17, 19, 29] compares reasonably well with the experiment below the percolation point, but fails to do so beyond the gel point, occurring at about weight 30% polymerization. [22]

These considerations lead us to conjecture that the critical scaling behaviour which we observe in the vicinity of the inflection point of Fig.1, and which is discussed in the next section, arises from the percolation of dense regions where the cage effect can be observed, and vitrification sets in. This also raises the possibility in Ref. [11], the critical scaling that is observed is due to the percolation of slow regions in this sense and may lead us to reassess our interpretation of the latter results.

IV. PERCOLATION OF SLOW REGIONS

We would like to cast the quasi-static properties of the polymer melt in the language of percolation, to interpret our results.

Note that free monomers are relatively easy-to-displace objects which do not constrain the motion of the large chains. By a slow region, we shall mean a region of sufficiently high density, such that parts of several chains, or even of the same chain, get in each other’s way and inhibit each other’s motion on a short time scale.

We take the volume fraction occupied by the total number of monomers incorporated into the chains as the “occupation probability,” \( p \), of the sites of a three dimensional lattice. We will take a cluster to be a set of occupied points on the lattice, which are nearest neighbor to at least one other member of the set. [11] Therefore such nearest neighbor occupied sites may be considered as belonging to the same cluster, regardless of whether they are chemically connected (i.e., belong to the same chain) or not. A spanning cluster of this description will be called a percolating cluster. We then argue that the pyrene molecules contributing to \( I \), the fluorescent intensity, are precisely those which are trapped within interstitial regions of these clusters.

If \( M \) is the average molecular weight of the chains,

\[
p = MCv_0/V \equiv v_0/v ,
\]

where \( C \) is the total number of chains, \( v_0 = V/N \) is the volume occupied by a single monomer, and \( N \) is the total number of monomers. The average length \( M \) of the chains obeys the differential equation

\[
\frac{dM(t)}{dt} = k(N - CM) ,
\]

over a sufficiently short time interval where the time dependence [22] of the reaction rate \( k \) due to the change in the viscosity, and of \( C \) (due to the gradual dissolution and termination of the initiators) can be neglected. Thus, for relatively short time intervals, we get a linear growth law,

\[
M(t) - M(t_0) = [M_\infty - M(t_0)] kC(t - t_0) .
\]

where \( M_\infty = N/C \) and \( t_0 \) is an arbitrary starting point. Defining \( t_c \) as the time at which the entanglement percolation threshold \( p_e \) is reached, and using Eq.(1), we have, for sufficiently small \( |t - t_c| \),

\[
|t - t_c| = \frac{1}{kC} \frac{p - p_e}{1 - p_e} \propto |p - p_e| .
\]

Since below \( t_c \), there is no percolating cluster, the total normalized fluorescent intensity will be proportional to the average cluster size \( S \). For \( t > t_c \), most of the pyrene molecules are trapped in the macroscopic network of slow regions, and \( I \) then measures the fraction \( P_\infty \) of the monomers that belong to the macroscopic cluster. [11]

For a system with linear size \( L \), the scaling forms for the quantities \( S \) and \( P_\infty \) around the percolation threshold, together with (4) yields,

\[
I \propto \begin{cases} S \sim (t_c - t)^{-\gamma} , & t < t_c \\ L^{d_f} P_\infty \sim L^{d_f} (t - t_c)^{\beta} , & t > t_c \end{cases} .
\]

Here, \( \beta \) and \( \gamma \) are the critical exponents for the strength of the infinite cluster and the average cluster size, and \( d_f = (\beta + \gamma)/\nu \) is the fractal dimension of the spanning cluster, with \( \nu \) being the correlation length exponent. [8] Notice that we need not subtract the value of \( I(t_c) \) from \( I(t) \) in (3) for \( t > t_c \) since we are assuming that once the threshold has been crossed, the unquenched fluorescence intensity is being contributed essentially by the monomers trapped in the incipient infinite cluster.

The time derivative of the intensity \( I \) is plotted in Fig. 2, and looks like a typical critical peak, with rounding due to “finite size” effects. The fits to the double logarithmic plots of the fluorescence intensity v.s. \( |t - t_c| \)
for $t > t_c$ and $t < t_c$, are shown in Fig. 3. The critical point $t_c$ and the exponents $\beta$ and $\gamma$ are determined by simultaneously fitting the intensity data to the behaviour in Eq. (6), in such a way as to obtain the greatest range in $|t - t_c|$ over which one finds scaling, both above and below the critical point. In this way it is possible to remove the ambiguity from the position of the critical point and greatly enhance the accuracy of the critical exponents. We see that the critical region is confined to the interval $3 < |t - t_c| < 30$. The values of the exponents are given in Table I. The agreement with the known values ($\beta = 0.41, \gamma = 1.80$) of the percolation exponents in three dimensions, is very good, with $\beta = 0.41 \pm 0.01$ and $\gamma = 1.7 \pm 0.1$. The error bars are estimated from the values reported in the table. The numbers for 60°C differ markedly from the rest and we have excluded them from our estimate of the exponents. At such low temperatures the mobility of the MMA are reduced to the point where the reaction ends before all the monomers are exhausted (the absolute intensity is lower at this temperature). The remaining monomers act as if a solvent were added to the bulk, increasing the lower length scale of the percolating network, and distorting the scaling behaviour. On the other hand, at 125°C the sample is boiling before the polymerisation has had time to progress, and the curve below the transition point is rather noisy, so that we find $\gamma = 1.4$; we recover $\beta = 0.41$ above the transition point.

The critical point $t_c$ obtained from the best scaling fits is smaller than $t_m$ marking the maximum of the $dI/dt$ curve. The quantity $c \equiv (t_m - t_c)/t_{1/2}$ where $t_{1/2}$ is the half–width of the $dI/dt$ curve at half maximum, is found to be

$$c \equiv \frac{t_m - t_c}{t_{1/2}} = 0.248 \pm 0.005,$$

(6)

over the whole range of experiments, and for different temperatures. This value is the same as that found from the measurements performed near the percolation transition found from fluorescence measurements on crosslinked gels [4].

Finite size scaling [4] predicts that this ratio is in fact a universal constant for percolation. From Eq. (6) we see that $dI/dt$ must obey the finite size scaling relations

$$\frac{dI}{dt} \sim L^{(\gamma+1)/\nu} \begin{cases} \phi_s'(t_c - t)L^{1/\nu} & t < t_c \\ \phi'_p[(t - t_c)L^{1/\nu}] & t > t_c \end{cases}$$

with the scaling functions $\phi_s(x) \sim x^{-\gamma}$ and $\phi_p(x) \sim x^{\beta}$ for $x \gg 1$, and $\sim \text{const.}$ for $x \ll 1$. Let us define the universal scaling function $\Phi'$ by $dI/dt \sim L^{(\gamma+1)/\nu}\Phi'(t - t_c)L^{1/\nu}$. Then $\Phi'$ clearly corresponds to the curve depicted in Fig. 2, both above and below $t_c$, and $c$ must be given in terms of its moments, $z_n = \int z^n \Phi'(z) dz$, as $c = z_1/(z_2 - z_1) \sim O(1)$. The fact that we find the same numerical value for $c$ as that determined from the cross-linking gelation experiment [1] is further indication that the transition we observe here is in the same universality class as percolation.

To understand this universality, we note that a dense region will look like a branching point under a coarse graining by some factor $b$, (while a bigger “blob” will now look like a tight entanglement region). If the percolating entanglement cluster is self-similar at length scales $\ell \ll \xi$, (where $\xi$ is the correlation length diverging like $|p - p_c|^{-\nu}$, near the percolation threshold), this transformation will simply renormalize $|p - p_c|$ by a factor $b^{1/\nu}$, but otherwise leave the scaling behaviour unaffected. Below the percolation threshold, the finite clusters themselves are fractal for $\ell \ll \xi$ and the same argument applies.

V. DISCUSSION

We have observed that steady state fluorescence experiments in a polymeric melt reveal a sharp transition in the narrow crossover region from low conversion to high conversion and vitrification. The transition is characterised by percolation exponents. On the basis of arguments presented in section 3, we believe that the critical scaling behaviour we observe in the fluorescent signal as...
a function of time is not due to the physical gelation of the sample due to entanglements, but to the percolation of dense regions where the cage effect constrains the local segmental motions of the linear chains and the radicals as well as the pyrene probe.

It is relevant to note in this context the dynamical scaling hypothesis [8], which asserts that, as the glass transition is approached from above, long range dynamical spatial correlations build up between particles of fragile glass formers. Dynamical clusters are formed out of those objects which have cooperatively rearranged, using the same free volume to accomplish the move. In the present context, this idea acquires particular significance, because with the onset of the “gel effect,” and the trapping of the free radicals, further polymerization must proceed in exactly the same way as the motion of a particle in a vitrifying medium, leaving behind, moreover, a permanent “trail” consisting of a long chain that is formed as a result. The chain can only grow if unattached monomers (which act like free volume with respect to monomers already incorporated into the chains) can exchange places with segments of neighboring chains trapping the radical at the head of the growing chain. Once a monomer is attached to the growing chain, a new monomer has now to exchange places with the surrounding chain segments, and will in turn be eaten up by the radical, etc. This process then leaves behind a growing chain confined within dense regions, and interconnecting these dense regions. The sudden rise in the rate of polymerization at the onset of the “gel effect” feeds on itself in nonlinear fashion, and suddenly gives rise to the percolation of dense, slow regions in the melt. The entrapment of the pyrene probe in these slow regions gives rise to the critical behaviour of the fluorescent intensity.

Acknowledgements

It is our great pleasure to acknowledge a very useful discussion with Prof. O. Okay. Y.Y., A.E. and Ö. P. would like to thank the Turkish Academy of Sciences for partial support.

[1] P.-G. de Gennes, Scaling Concepts in Polymer Physics, (Cornell University Press, Ithaca, 1988), pp.54.
[2] M. Doi and S.F. Edwards, The Theory of Polymer Dynamics (Clarendon, Oxford, 1986).
[3] W. Goetze, “Aspects of Structural Glass Transition,” J.-P. Hansen and J. Zinn-Justin eds., Les Houches, Session LI, 1989, Liquids, Freezing and Glass Transition, (Elsevier, Amsterdam, 1991).
[4] http://www.kemcointernational.com/AcrylicResins.htm
[5] Y. Yilmaz, O. Pekcan and A. Erzan, “Percolation exponents at the entanglement transition of a linear polymer,” cond-mat/0111337.
[6] D.S. Achilias and C. Kiparissides, Macromolecules, 25 3739 (1992); M. Cioffi, A.C. Hoffmann, L.P.R.M. Janssen, Nonlin. Analysis 47, 897 (2001); L. Gu, S. Zhu, A.N. Hrymak and R.H. Polon, Polymer 42, 3077 (2001); see J.G. Qiu, W.P. Guo and Z.Zhang, Polymer 43, 1163 (2002) for more references.
[7] M.H. Cohen and G.S. Grest, Phys. Rev. B 20, 1077 (1979).
[8] R.H. Colby, Phys. Rev. E 61, 1783 (2000).
[9] P.H. Poole, C. Donati, S.C. Glotzer, Physica A 261, 51 (1998).
[10] C. Bennemann, C. Donati, J. Baschnagel, S.C. Glotzer, Nature 399, 246 (1999).
[11] Y. Yilmaz, A. Erzan, and O. Pekcan, Phys. Rev. E 58, 7487 (1998).
[12] Subsequently, a fast transient fluorescence technique has yielded the same exponents for the gelation transition in styrene. D. Kaya, O. Pekcan, and Y. Yilmaz, “Fast transient fluorescence technique to study critical exponents at the sol-gel phase transition,” Phase Transitions, in press.
[13] Ö. Pekcan and Y. Yilmaz “Fluorescence Method for Monitoring Gelation and gel Swelling in Real Time,” in Applied Fluorescence in Chemistry, Biology and Medicine, Eds. W. Rettig, B. Strehmel, S. Schrader (Springer-Verlag, Berlin, 1999), p. 371.
[32] L.J. Fetters, D.J. Lohse, D. Richter, T.A. Witten, and A. Zirkel, Macromolecules, 27, 4639 (1994).
[33] W. Paul, K. Binder, D.W. Heerman, K. Kremer, J. Phys. II 1, 37 (1991).
[34] W. Paul, K. Binder, D.W. Heerman, K. Kremer, J. Chem. Phys. 95, 7726 (1991).
[35] http://www.chemicalland21.com/arokorhi/industrial_chem/functional%20Monomer/METHYL%20METH-ACRYLATE.htm
[36] A.L. Kholodenko, Macromol. Theor. Sim. 5, 1031 (1996).
[37] O. Okay, Polymer 35, 796 (1994).
[38] O. Okay, Polymer 35, 2613 (1994).
[39] O. Okay, D. Kaya, O. Pekcan, Polymer 40, 6179 (1999).
[40] S. Zhu, Y. Tian, A.E. Hamielec, and D.R. Eaton, Polymer 31, 154 (1990).
[41] G.A. O’Neill and J.M. Torkelson, Macromolecules 32, 411 (1999).
[42] Y. Tian, S. Zhu, A.E. Hamielec, D.B. Fulton, and D.R. Eaton, Polymer 33, 384 (1992).
[43] A. Saiani, J. Spevacek, and J.M. Guenet, Macromolecules 31, 703 (1998).
[44] I. Erukhimovich, M.V. Thamm, and A.E. Ermoshkin, Macromolecules 34, 5653 (2001).
[45] D. Stauffer and A. Aharony, Introduction to Percolation Theory, (Taylor and Francis, London, 1992).
[46] D. Stauffer, A. Coniglio, and M. Adam, Adv. Polym. Sci. 44, 103 (1982).
[47] H. Herrmann, D.P. Landau, D. Stauffer, Phys. Rev. Lett. 49, 412 (1982).
[48] H. Herrmann, Phys. Rep. 136, 153 (1986).
[49] D. Balcan, A. Erzan, “MC Renormalization group calculation the for entanglement percolation of linear chains,” in preperation.
[50] P. F. Jones and S. Siegel, J. Chem. Phys. 50,1134 (1969).
[51] C.-Y. Wang and M.D. Ediger, Macromolecules 30, 4770 (1997).
[52] M.T. Cicerone, P.A. Wagner, and M.D. Ediger, J. Phys. Chem B 101, 8727 (1997).
[53] W. Zhu and M.D. Ediger, Macromolecules 30, 1205 (1997).
[54] C.-Y. Wang and D. Ediger, J. Phys. Chem. 104, 1724 (2000).
[55] J.-W. Park, M.D. Ediger, M.M. Green, J. Amer. Chem. Soc. 123, 49 (2001).
[56] We are indebted to Prof. G.H. Fredrickson for this comment.
[57] J.G. Kloosterboer, G.M.M. van de Hei, and H.M.J. Boots, Polymer Comm. 25, 354 (1984).
[58] J.G. Kloosterboer, G.M.M. van de Hei, R.G. Gossink, and G.C.M. Dortant, Polymer Comm. 25, 322 (1984).
[59] H.M.J. Boots and R.B. Pandey, Polym. Bull. 11, 415 (1984).