A blob model to parameterize
polymer hole free volumes and solute diffusion

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1 Apparent activation energies of linear solutes with anchors

Eq. (30) of the main document relates the diffusion coefficient of a linear and flexible solute including an anchor of molecular mass M_{anchor}, denoted $D_a(M,T)$, with the one of a similar solute without anchor and of molecular mass M, denoted $D(M,T)$. The ratio of diffusion coefficients is recast as:

$$\frac{D_a(M,T)}{D(M,T)} \approx \exp\left(-\frac{M_{anchor}}{M_{anchor}+M}\frac{E_a^{anchor}(T)}{RT}\right)\left(\left(\frac{M_{anchor}}{M}+1\right)\left(\frac{M_{anchor}+M}{M_{anchor}+M_{blob}}\right)^{\frac{M_{anchor}}{M}}\right)^{-\alpha_{lin}(T)} \quad \text{(S1)}$$

$$= A_{E_{a,a}}^{nFV}(M,T)\cdot B_D^{FV}(M,T)^{-\alpha_{lin}(T)}$$

The exponential term, denoted $A_{E_{a,a}}^{nFV}(M,T)$, represents the activation term not related to free volume (FV) effects; it describes the slowdown of the diffusion due to specific interactions between the anchor and the polymer mainly. This effect is assumed to occur randomly without hampering the displacements of the connected blobs. This condition is well verified when the solute center-of-mass is sufficiently far from the center-of-mass of the anchor itself. The second term $B_D^{FV}(M,T)$ is associated to the scaling exponent $\alpha_{lin}(T)$ and encompasses all free-volume effects acting on the displacements of connected blobs. In this description, all blobs and the anchor are assumed to be blocked independently of each other (independence of trapping times).

When the specific energy barrier E_{anchor}^a has essentially an enthalpic nature, it can be guessed as $E_a^{anchor} \approx \langle E_{a,a}(M=0,T)\rangle$, as discussed in §2. It is worth noticing that the proposed approximation does not imply that $D_a(M=0,T)$ is an estimate of the diffusion coefficient of the anchor itself,

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which is not generally true. Indeed, the translations of the center-of-mass of the isolated anchor and of the anchored solute obey to different dynamics.

Combining Eqs. (20) and (21) in the original with Eq. (S1) lead to the practical expression of the apparent activation energy for an anchored linear solute, $\langle E_{a,a} \rangle$:

$$\langle E_{a,a}(M,T) \rangle = \left\langle RT^2 \left. \frac{\partial \ln D_a(M,T)}{\partial T} \right|_M \right\rangle$$

$$= RK_\alpha \langle I \rangle \left(\frac{M_{anchor}}{M} \ln \left(\frac{M_{anchor}+M}{M_{anchor}+M_{blob}} \right) + \ln \left(\frac{M_{anchor}}{M}+1 \right) + \ln \frac{M}{M_{blob}} \right) +$$

$$\langle E_a(M_{blob}) \rangle + \frac{M_{anchor}}{M_{anchor}+M} E_a^{anchor} \quad\quad\quad\quad (S2)$$

$$= RK_\alpha \langle I \rangle \left(\frac{M_{anchor}}{M} \ln \left(\frac{M_{anchor}+M}{M_{anchor}+M_{blob}} \right) + \ln \left(\frac{M_{anchor}+M}{M_{blob}} \right) \right) +$$

$$\langle E_a(M_{blob}) \rangle + \frac{M_{anchor}}{M_{anchor}+M} E_a^{anchor}$$

1.1 Scaling with M_{blob}

For $M = M_{blob}$, Eq. (S2) becomes:

$$\langle E_{a,a}(M_{blob},T) \rangle = RK_\alpha \langle I \rangle \ln \left(1 + \frac{M_{anchor}}{M_{blob}} \right) + \langle E_a(M_{blob}) \rangle + \frac{M_{anchor}}{M_{anchor}+M_{blob}} E_a^{anchor} \quad (S3)$$

For $M = 2M_{blob}$, Eq. (S2) becomes:

$$\left\langle E_{a,a}\left(2M_{blob},T\right)\right\rangle = RK_{\alpha}\left\langle I\right\rangle\left(\frac{1}{2}\frac{M_{anchor}}{M_{blob}}\ln\left(1+\frac{M_{blob}}{M_{anchor}+M_{blob}}\right)+\ln\left(2+\frac{M_{anchor}}{M_{blob}}\right)\right)+$$

$$\left\langle E_a\left(M_{blob}\right)\right\rangle + \frac{M_{anchor}}{M_{anchor}+2M_{blob}}E_a^{anchor}$$

$$\approx RK_{\alpha}\left\langle I\right\rangle\left(\frac{1}{2}\frac{M_{anchor}}{M_{anchor}+M_{blob}}+\ln\left(2+\frac{M_{anchor}}{M_{blob}}\right)\right)+$$

$$\left\langle E_a\left(M_{blob}\right)\right\rangle + \frac{M_{anchor}}{M_{anchor}+2M_{blob}}E_a^{anchor}$$

(S4)

The difference of activation energy between two anchored molecules connected respectively to one and two blobs, is linearized as:

$$\left\langle E_{a,a}\left(2M_{blob},T\right)\right\rangle - \left\langle E_{a,a}\left(M_{blob},T\right)\right\rangle$$

$$= RK_{\alpha}\left\langle I\right\rangle\left(\frac{1}{2}\frac{M_{anchor}}{M_{blob}}\ln\left(1+\frac{M_{blob}}{M_{anchor}+M_{blob}}\right)+\ln\left(1+\frac{M_{blob}}{M_{anchor}+M_{blob}}\right)\right)-$$

$$\frac{M_{blob}M_{anchor}}{\left(M_{anchor}+M_{blob}\right)\left(M_{anchor}+2M_{blob}\right)}E_a^{anchor}$$

$$\approx RK_{\alpha}\left\langle I\right\rangle\ln\left(1+\frac{M_{blob}}{M_{anchor}+M_{blob}}\right)\left(\frac{1}{2}\frac{M_{anchor}}{M_{blob}}+1\right)-$$

(S5)

$$\frac{M_{blob}M_{anchor}}{\left(M_{anchor}+M_{blob}\right)\left(M_{anchor}+2M_{blob}\right)}E_a^{anchor}$$

$$\approx \frac{1}{2}RK_{\alpha}\left\langle I\right\rangle\frac{M_{anchor}+2M_{blob}}{M_{anchor}+M_{blob}}-$$

$$\frac{M_{blob}M_{anchor}}{\left(M_{anchor}+M_{blob}\right)\left(M_{anchor}+2M_{blob}\right)}E_a^{anchor}$$

The equation of $\left\langle I\right\rangle$ is given by Eq. (19) of the main document.

1.2 Scaling with M_{anchor}

Eq. (S3) is used similarly to scale the apparent activation energy, $\left\langle E_{a,a}\right\rangle$, with the mass of the anchor, M_{anchor}, independently of the length of the alkyl chain connected to it. The difference of activation energies between two solutes A and B, differing only by the molecular mass of the anchor, denoted M_{anchor}^A and M_{anchor}^B, respectively, is given by:

$$\left\langle E_{a,a}\left(M_{anchor}^{B}, M, T\right)\right\rangle - \left\langle E_{a,a}\left(M_{anchor}^{A}, M, T\right)\right\rangle$$

$$= RK_{\alpha}\left\langle I\right\rangle \left(\begin{array}{c} \dfrac{M_{anchor}^{B}}{M}\ln\left(\dfrac{M_{anchor}^{B}+M}{M_{anchor}^{B}+M_{blob}}\right) - \dfrac{M_{anchor}^{A}}{M}\ln\left(\dfrac{M_{anchor}^{A}+M}{M_{anchor}^{A}+M_{blob}}\right) \\ + \ln\left(\dfrac{M_{anchor}^{B}+M}{M_{anchor}^{A}+M}\right) \end{array} \right) + \qquad \text{(S6)}$$

$$\dfrac{M_{anchor}^{B}}{M_{anchor}^{B}+M}E_{a}^{B,anchor} - \dfrac{M_{anchor}^{A}}{M_{anchor}^{A}+M}E_{a}^{A,anchor}$$

When $M = M_{blob}$, one gets:

$$\left\langle E_{a,a}\left(M_{anchor}^{B}, M = M_{blob}, T\right)\right\rangle - \left\langle E_{a,a}\left(M_{anchor}^{A}, M = M_{blob}, T\right)\right\rangle$$

$$= RK_{\alpha}\left\langle I\right\rangle \ln\left(\dfrac{M_{anchor}^{B}+M_{blob}}{M_{anchor}^{A}+M_{blob}}\right) + \dfrac{M_{anchor}^{B}}{M_{anchor}^{B}+M}E_{a}^{B,anchor} - \dfrac{M_{anchor}^{A}}{M_{anchor}^{A}+M}E_{a}^{A,anchor} \qquad \text{(S7)}$$

2 Comparison with experiments

Conversely to cases described in the main document, we propose here to analyze the effect of the anchor when it is maximized, that is when $M_{anchor} > M$. When the number of blobs, N, is very low ($0 \le N \le 4$), it is, however, preferable to choose M_{blob} commensurable to CH_2 instead of CH_2CH_2 (the latter was chosen in the main document). Three direct comparisons with experiments are proposed and discussed.

- (§2.1.1) Comparison of Eq. (S1) with the experimental ratios of diffusion coefficients alkylbenzenes (internal data) and *n*-alkanes (this work) in PET at 373 K; the final goal of the comparison is to conclude on the importance of E_a^{anchor} (benzyl group) in the diffusion of toluene, ethylbenzene, etc. in a semi-aromatic polymer.

- (§2.1.2) Contribution of the same benzyl group on $\left\langle E_{a,a}\left(M\right)\right\rangle$ in an aromatic polymer (PS, temperature range: 383 K-413 K, data from Ref. [1] and its comparison with the theoretical excess activation energy (free-volume effect) of one single blob as predicted by Eq. (S5).

- (§2.2) Comparison between the theoretical effect of M_{anchor} in an aliphatic polymer (PMMA, temperature range: 362 K-444 K; data are from Ref. [1]) and apparent activation energies when anchored solutes include a single aliphatic blob. This dataset is used to demonstrate that E_a^{anchor} is likely to decrease with M_{anchor} and the likeliness of a specific interaction with the polymer.

2.1 Diffusion of alkylbenzenes

2.1.1 Diffusion in a semi-aromatic polymer (PET): extrapolation of $D_a(M,T)$ values from $D(M,T)$ using $E_a^{anchor} \approx 0$

The first comparison relies on two datasets (*n*-alkanes and alkylbenzenes) measured by the same group using in similar conditions (permeation experiments) and in the same polymer at 373 K. As the number of blobs (here CH_2) was higher in *n*-alkanes ($N \geq 3$) than in alkylbenzenes ($N = 1.4$), a linear scaling of $\ln D$ with $\ln N$ was used to enable a comparison on the full range of alkylbenzene. The ratios $\frac{D_a(M,T)}{D(M,T)}$ calculated from Eq. (S1) are compared with experimental values in Figure S1 when E_a^{anchor} is neglected ($A_{E_{a,a}}^{nFV}(M,T) \approx 1$).
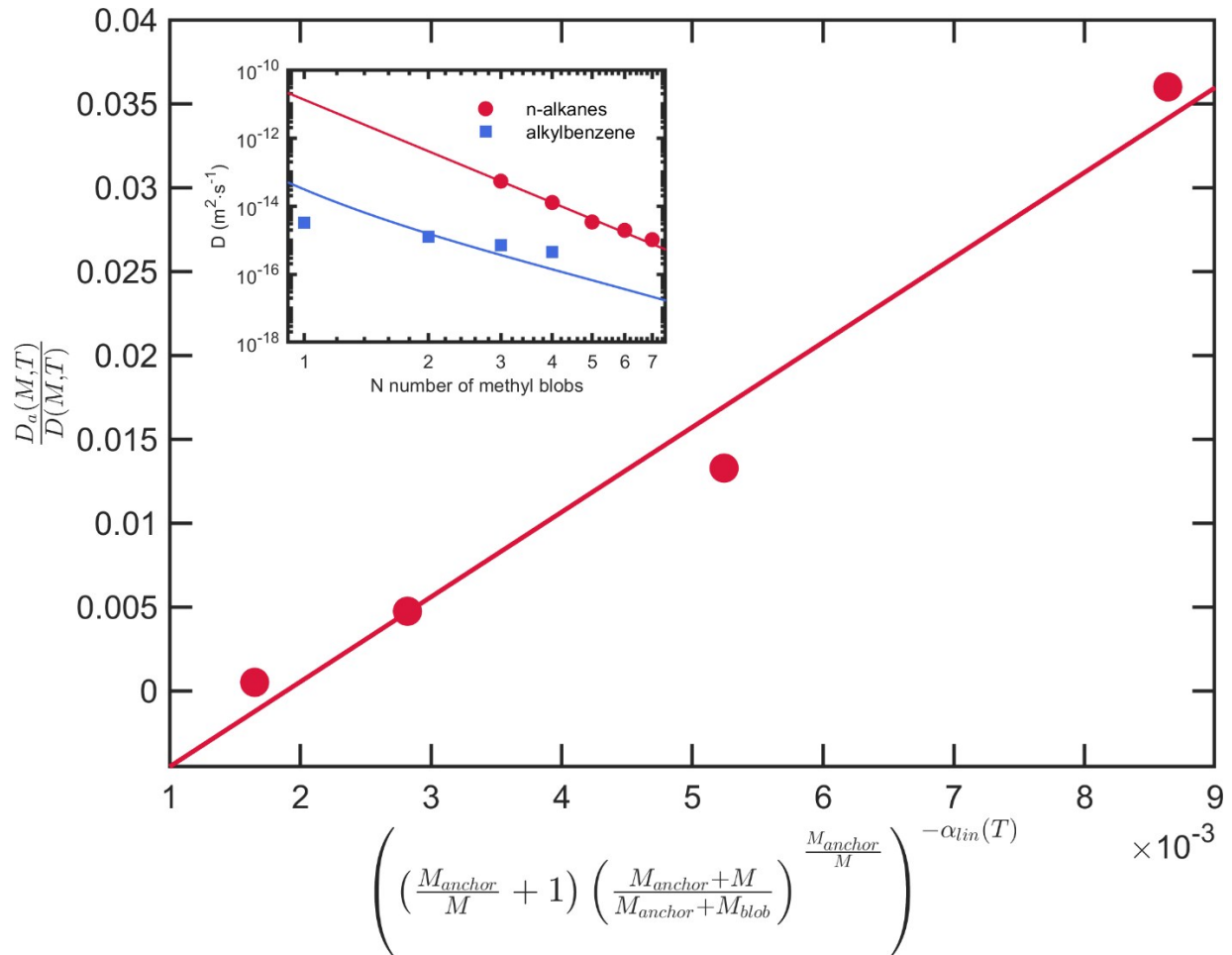

Figure S1. Comparison of the experimental ratio of diffusion coefficients of alkylbenzenes (D_a, internal data)-to-alkanes (D, this work) in PET at 373 K with Eq. (S1) when the specific activation term, E_a^{anchor}, is neglected. Other parameters are $M_{blob} = 14$ g·mol^{-1} and $M_{anchor} = 79$ g·mol^{-1}. The inset plots the linear scaling of n-alkanes along the prediction of D_a from Eq. (30).

A linear behavior is obtained with a slope slightly greater than unity, which confirms the absence of specific interactions between a benzyl group and PET segments. Non-linear fitting of Eq. (S1) gives indeed $E_a^{anchor} \approx \pm 1$ kJ·mol⁻¹ without improving significantly the quality of the fit. The direct comparison of Eq. (30) with experimental is shown in the inset of Figure S1. The deviation is more obvious and shown a lower effect of N (equivalently M) on D_a experimental values than suggested by theory. It is argued that the center-of-mass of short alkylbenzenes is not sufficiently separated from the one of benzyl to enable a full independence of the cycle of trapping/release of each blob (here CH₂) and of the benzyl group.

2.1.2 Diffusion in an aromatic polymer (PS): extrapolation of $\langle E_a \rangle$ from benzene value

Alkylbenzenes in rubber polystyrene are likely to be highly sensitive to π-π interactions and π-stacking [2]. The associated trapping is different in nature from the entropic nature of the constrain/release mechanism initially envisioned for alkyl blobs and benzyl anchor in non-aromatic polymers. We combine here the apparent activation energies of benzene, toluene, ethylbenzene within a double attempt of combining Eq. (S5) and of testing the approximation $E_a^{anchor} \approx \langle E_{a,a}(M=0,T) \rangle$.

Reference experimental diffusion coefficients were from Ref. [1] and were obtained at infinite dilution by inverse gas chromatography (between 383 K and 413 K). The apparent activation energy of toluene given reported independently in Ref. [3] in amorphous PS is used as reference to predict the one of benzene and ethylbenzene. The negative and positive increment is calculated from the linear approximation Eq. (S5) and was estimated to 13 kJ·mol⁻¹.

The predictions are remarkable, in particular, for benzene and demonstrated that in this case, the value of E_a^{anchor} was very significant, and one magnitude order larger than the contribution of one single blob due to FV effects. Similar effects are expected to occur with H-bonding in polar polymers, as shown in §2.
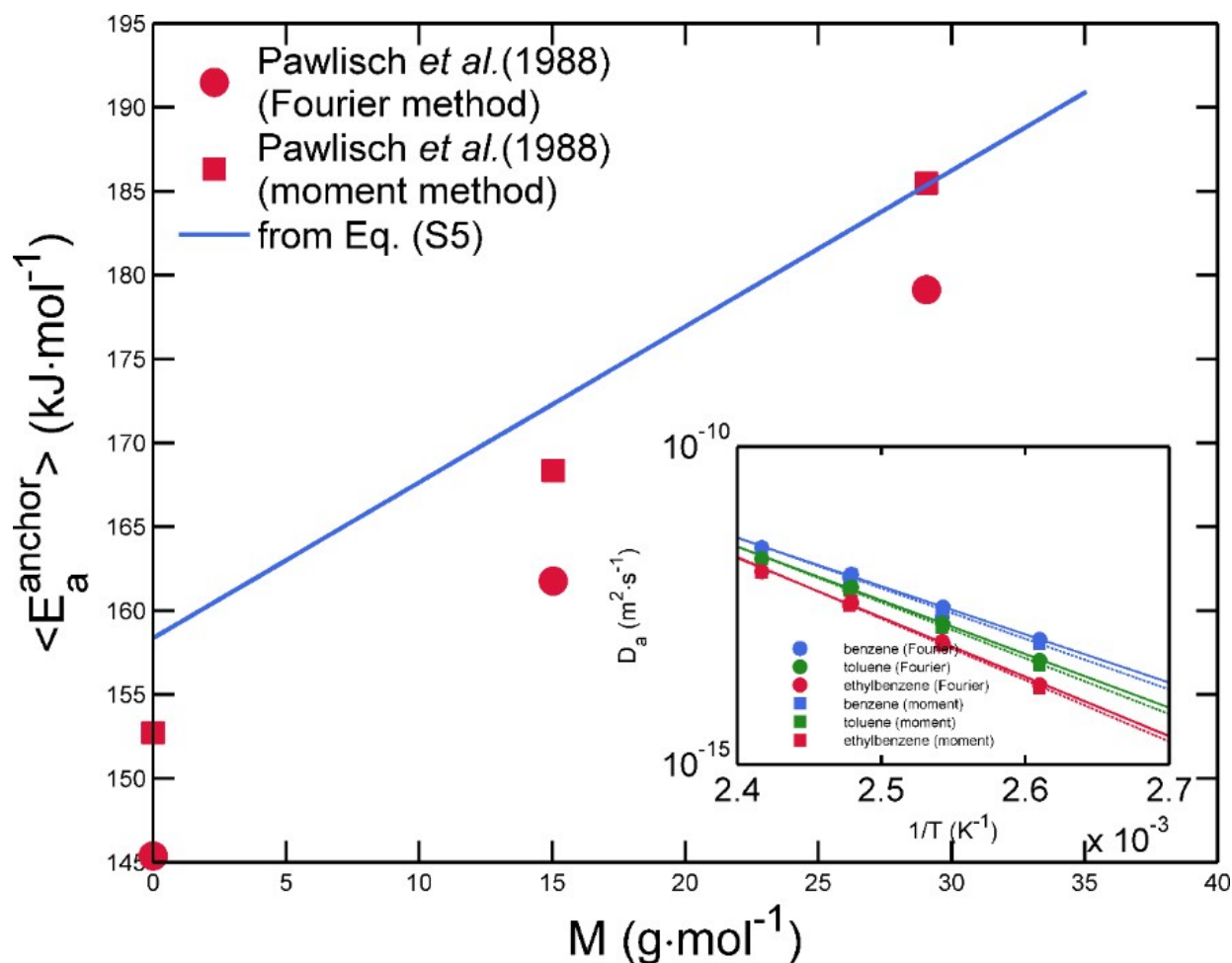
Figure S2. Effect of the side alkyl chain length (M) on apparent activation energies of benzene, toluene, and ethylbenzene in polystyrene (data from Ref. [1]). The linear model assumes an increment of activation energy between toluene and ethylbenzene given by Eq. (S5) with K_α and K_β equal to 150 K and 40 K, as reported in Ref.[4].The value for toluene matches the theoretical value reported for toluene by Vrentas et al. [3]. The inset depicts the experimental D_a values obtained by inverse gas chromatography from both the moment and Fourier methods (see Ref. [1] for details).

2.2 Effect of M_{anchor} and specific polymer interactions in polar aliphatic polymers: difference between estimated and apparent activation energies when E_a^{anchor} is neglected

PMMA is proposed as a weakly polar host matrix, where specific polar and H-bonding interactions can occur between polymer segments and the tested anchor. Three solutes, methanol, methyl acetate and methyl methacrylate, were assumed to be part a same homologous series with increasing in size anchors. The alkyl chain is, indeed, commensurable to one single CH_3, and the remaining chemical group (alcohol, acetate, methacrylate) plays the role of the anchor. The experimental reference values were inferred from D values reported in Ref. [1]. The apparent activation energy of methanol reported independently in Ref. [5] along Eq. (S7) was used to extrapolate the activation energies of the two solutes following methanol. The results obtained with the initial guess $E_a^{anchor} \approx 0$ are compared with experimental values in Figure S3.
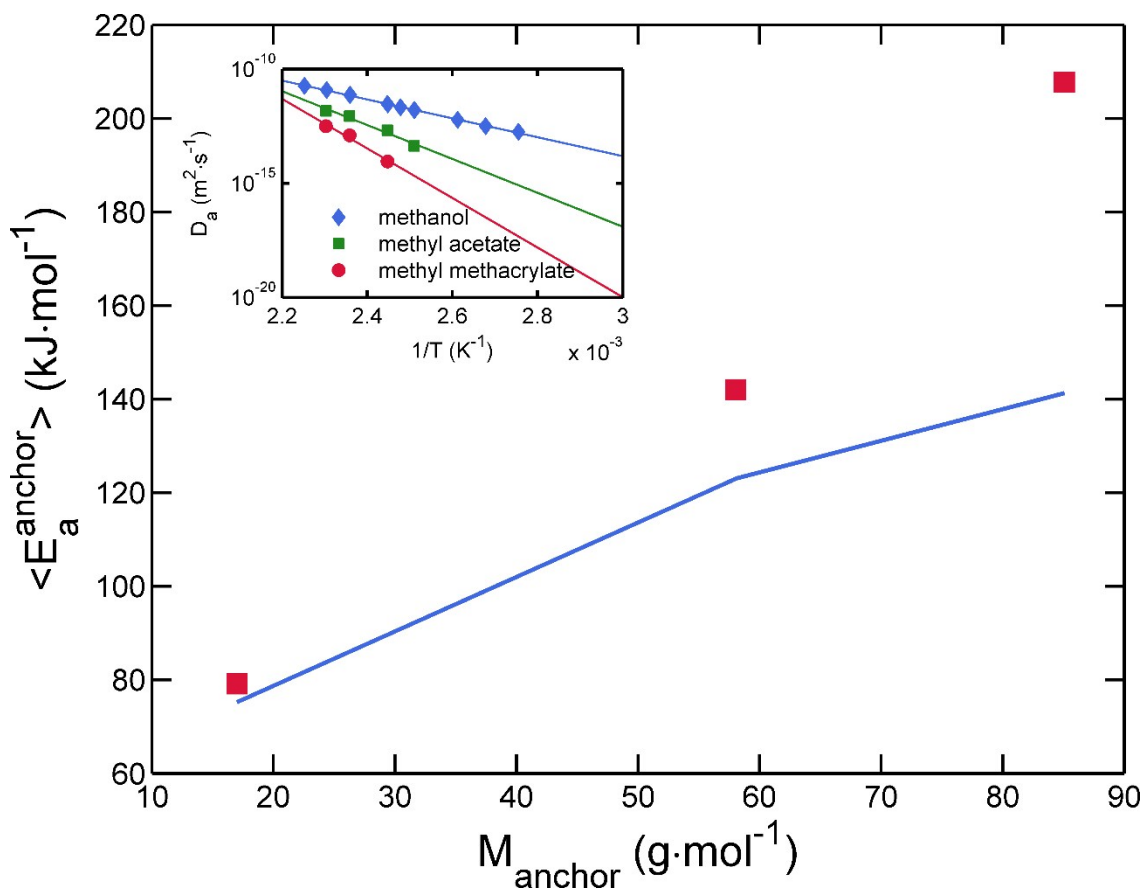

Figure S3. Effect of the anchor mass (M_{anchor}) on apparent activation energies of methanol, methyl acetate, and methyl methacrylate in poly(methyl methacrylate). Experimental data from Ref.[1] (symbols) are compared with the extrapolations from Eq. (S7) at similar temperatures. The value of methanol of Ref. [5] was chosen as reference to see Eq. (S7). The values of K_α =150 K and K_β =40 K reported in Ref.[4] were used for the predictions. The inset depicts the raw experimental data used to infer apparent activation energies.

The positive difference between the experimental values and the theoretical ones can be, therefore, interpreted as a guess of E_a^{anchor}. The estimates are ca. 25 and 70 kJ·mol^{-1} for methyl acetate and methyl methacrylate, respectively. They represent 1:7 and 1:3 of the total apparent activation energies. This contribution is not as high as in PS but it demonstrates that E_a^{anchor} can affect dramatically the diffusion and its activation by temperature for small solutes.

The detailed examples show that solutes including large and/or interacting anchors are not good molecular probes to assess FV effects. Their use should be, therefore, avoided. The contribution of the hydroxyl group in a solute as small as methanol in PMMA was estimated to less than 10% of the total activation energy. Large 1-alcohols, as depicted in Figures 2a-c, of the main document are acceptable as molecular probes either in isothermal (via the scaling exponent α_a) or anisothermal interpretations (via $E_{a,a}$). Using the behavior of short alkyl acetates in PVAc (see Figure 1d) with temperature to probe FV effects should be, conversely, proscribed.

3   References

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