Environmentally Sensitive Luminescence Reveals Spatial Confinement, Dynamics and Their Molecular Weight Dependence in a Polymer Glass

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KEYWORDS: luminescence, confinement, responsive polymers, glass transition, copper

ABSTRACT: Polymer glasses have an irregular structure. Among the causes for such complexity are the chemically distinct chain end-groups that are the most abundant irregularities in any linear polymer. In this work we demonstrate that chain end induced defects allow polymer glasses to create confined environments capable of hosting small emissive molecules. Using environmentally sensitive luminescent complexes we show that the size of these confinements depends on molecular weight and can dramatically affect the photoluminescence of free or covalently bound emissive complexes. We confirm the impact of chain end confinement on the bulk glass transition in poly(methyl acrylate) and show that commonly observed T_g changes induced by the chain ends should have a structural origin. Finally, we demonstrate that size and placement of luminescent molecular probes in pMA can dramatically affect the probe luminescence and its temperature dependence suggesting that polymer glass is a highly irregular and complex environment marking its difference with conventional small molecule solvents. Considering the ubiquity of luminescent glassy materials, our work lays down a blueprint for designing them with structural considerations in mind, ones where packing density and chain end size are key factors.

Introduction

Polymers are highly complex materials from a structural and a dynamic point of view. A local, molecular level characterization of such complexity in polymers and soft matter can be achieved using small molecule probes that can be placed within materials and provide information about its surroundings. Several approaches to probe-based techniques gained traction in the last decades. Historically, one of the first practices in the field employed probes for fluorescence spectroscopy correlation studies. Using these fluorophores it was possible to track molecular mobility and dynamic heterogeneity in polymer glasses[1-7] and characterize chain dynamics[8] and local viscosity.[9] Stable luminescence is one of the main requirement for correlation spectroscopy probes that are otherwise environmentally insensitive, i.e. their luminescence varies marginally when the polymer environment changes.

Alternative characterization approach utilizes molecular probes with environmentally sensitive luminescence. Such probe molecules can, for example, vary their emission color or intensity in response to changes of polymer aggregation state, viscosity and free volume characteristics.[10-17] While these probes can be more chemically complex, they often provide a simple color or intensity based response that is easy to detect and analyze. Perhaps the most illustrative of the practice is the recent report by Christie, Register and Priestley[18] who used a simple pyrene dye to perform local T_g analysis in block copolymers. These authors demonstrated that local T_g can vary significantly, by tens of degrees, in lamellar PMMA/PBMA block copolymers within the space of several nanometers.

The latter work demonstrates the importance of probe placement chemistry for interpreting the photoluminescence (PL) data. Since different parts of material can exhibit different extent dynamics, even a common choice between tethered[18-19] or freely dispersed probes defines which space in the polymer will be accessible to the probe molecules and which aspect of polymer dynamics they will ultimately describe. This touches on the principal questions one should ask when using responsive small molecules: How informative are local probe-based measurements and which local and bulk material features do they report?[12]

In this work we demonstrate that by controlling the structure and placement of molecular probes one can distinguish between their local and global mode of operation. This approach reveals pronounced differences in glass transition behavior of the polymer bulk and the chain end groups and connects the latter to the free volume characteristics of the parent polymer that are shown to be molecular weight dependent. Importantly, we show how minor variations, benign from a synthetic chemistry standpoint, have a dramatic impact on the probe luminescence.

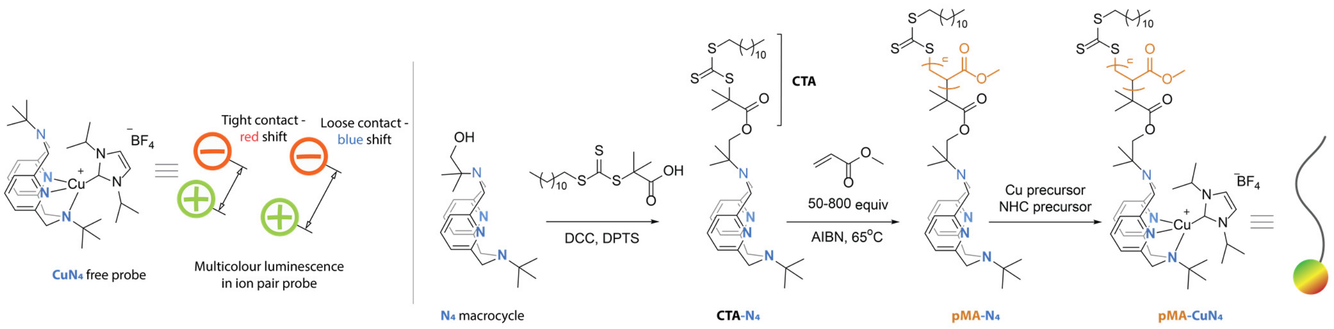

Figure 1. Structure of the $\mathbf{CuN_4}$ probe and synthesis of end-labelled pMA samples **pMA-**$\mathbf{CuN_4}$;

We point out that such variations in luminescence color have structural origin, carry information about the environment surrounding the emissive complexes and can generally occur in any polymer glass blended with emissive molecules.

As the majority of molecular probes are several dozens of atoms in size, we center this work around a similarly sized irregularity found in any linear polymer – the polymer chain end groups. While being a small fraction of the polymer, the chemical structure of the end groups is known to impact the bulk T_g. An example of this behavior has recently been demonstrated by Torkelson and coworkers[20] who reported T_g perturbations of nearly 35K for polystyrene samples of M_n ~ 4kDa with chemically distinct end groups. Conceptually, end groups can be viewed as packing defects in a polymer melt or glass, having, as a consequence, higher available free volume compared to the rest of the chain.[21] The contribution of chain ends and their number or concentration per unit volume is central to explaining the molecular weight (M_n) dependence of polymer properties, e.g. viscosity or glass transition temperature. A well-known model that illustrates this was postulated by Flory and Fox.[22-23] In practice, it suggests that polymers with lower molecular weight and thus high chain end concentration typically have a lower T_g that saturates to an asymptotic value as M_n increases. Interestingly, in cyclic polymers having no chain ends the $T_g(M_n)$ dependence is largely supressed[24-26] and low M_n cyclic polystyrenes[27-28] are barely distinguishable by their T_g from cyclic PS of higher molecular weights.

These data highlights connection between the local polymer structure at the chain end groups and the glassy behavior of the bulk. Furthermore, the chain ends appears to be central to the establishment of M_n dependence of the polymer properties noted above. Assuming this phenomenon to have a structural origin we set out to test the capacity of molecular probes for studying the microscopic structure of glasses with the ultimate goal of connecting microscopic their features with the bulk behavior.

Results and Discussion

In this work, we utilized a family of thermochromic phosphorescent probes recently developed by our group for ratiometric color-based bulk T_g characterization.[29] Unlike the majority of emissive probes used, for example, in the fluorescent correlation spectroscopy studies,[3, 19] the CuN_4 probes (Figure 1) used in this work are designed to probe the material dynamics on the timescale of the probe photoluminescence (PL). Namely, the PL spectrum of CuN_4 and its emission color is linked to the ion pair geometry within the probe molecule.[30] Photoexcitation of CuN_4 triggers a structural rearrangement of this ion pair which is strongly dependent on the mobility of the polymer hosting the probe (Figure 2). In the case of immobile ion pairs, like the ones found in a polymer glass, the ion pair distance is largely controlled by the local glass structure and its thermal expansion. In a polymer melt the ion pair is mobile and can rearrange towards the equilibrium excited state geometry where the rate of this rearrangement controlled by ion mobility. This creates peculiar PL color dependence for CuN_4 in glass forming polymers that we visualize by plotting PL color as spectral intensity ratio *I(530)/I(610)* versus sample temperature (Figure 2C). Three distinct regions of the ratiometry[29] curve describe the relation between temperature and ion pair motions in the polymer host. In a glassy environment the emission color varies monotonically until the polymer is sufficiently mobile to allow ion pairs to rearrange. This point is characterized by a distinct change in the PL spectrum showing a local maximum in the ratiometry curve that marks the onset of the mobility associated with glass transition, we will refer to this temperature as PL onset temperature Further increase in temperature accelerates the ion diffusion making it sufficiently fast to take place within the lifetime of the probe excited state. At this temperature the ratiometry curve recovers a positive slope which is marked by a local minimum that we previously referred to as the *dynamic* T_g as it occurred on characteristic timescales of microseconds.[29]

Our initial aim was to target CuN_4 probes to the polymer end groups that can be done in a multi-step synthesis. We firstly prepared a series of chain end labelled poly(methyl acrylate) samples incorporating the N_4 ligand at the chain end using RAFT polymerization technique (**pMA-**$\mathbf{N_4}$, Figure 1). The polymer samples of M_n varying from 4 kDa to 53 kDa were further treated with Cu metal precursor to convert N_4 ligand to luminescent copper complex (**pMA-**$\mathbf{CuN_4}$, Figure 1). NMR spectroscopy confirmed the identity of resulting species at every step of polymer synthesis indicating incorporation of macrocyclic ligand at the terminal site of the pMA chain and its further conversion to the charged luminescent Cu complex (See Supporting Information). Post metalation, polymer samples were drop cast from solution, conditioned at T>T_g and the temperature dependence of their luminescence was analyzed.

We found the luminescence of all CuN_4 labelled polymer samples was temperature dependent. We specifically noted the strong M_n dependence of probe luminescence in the glassy state. Comparing the PL spectra recorded at -90°C (Figure 2a), we observed significantly red shifted probe emission in low M_n polymers compared to that in high M_n samples. This color variation is somewhat unexpected as it occurs in a set of chemically identical polymers and emissive complexes of identical chemical structure.

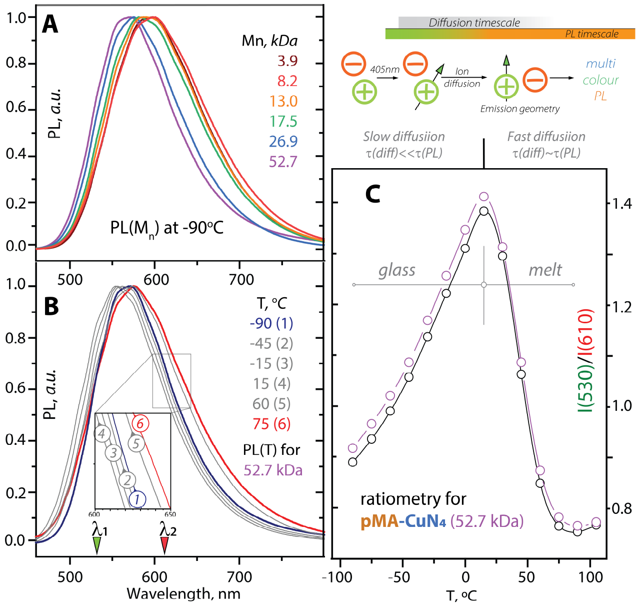

Figure 2 (A) Molecular weight dependence of emission spectra of end-labelled pMA in the glassy state at -90°C; (B) Thermochromism of end labelled pMA with M_n=52.7 kDa at selected temperatures with wavelengths used for ratiometry analysis indicated – λ1=530 nm, λ2=610 nm; (C) Ratiometric data for pMA with M_n=52.7 kDa, duplicate measurements shown.

Rationalizing these PL differences we recall that PL color in CuN_4 is controlled by the ion pair spacing,[29-30] which suggests that pMA of different molecular weight confines the probe molecules differently. Specifically, the red shift of PL spectrum observed in low M_n pMA implies a more tight ion pairing compared to that in high M_n pMA. This indicates that the volume around the chain end available for confinement is lower in low M_n pMA and gradually increases with increase of M_n.

This directly links the observed probe confinement effects to the free volume characteristics of polymer glasses and implies that the free volume element (FVE) size in pMA is M_n dependent and decreases for higher M_n. While unusual, this idea finds support from literature suggesting that the FVE size does decrease with increasing molecular weight at least for polystyrene.[31] In addition, the concept of packing density dependence on chain length is well documented on the macroscopic scale. For example, Zou et al. have drawn similarities between temperature dependence of T_g and chain packing density and using a macroscopic granular chain model demonstrated that higher density packings are indeed formed by shorter chains.[32] Finally, the recent data from Fayer and co-workers suggests that CuN_4 sensors might indeed occupy FVEs in the polymer. Authors found the sizes of FVE in PS and PMMA to span the range of 5-8 Å making them at least partially accessible for CuN_4 probes sized in the same extent.[33]

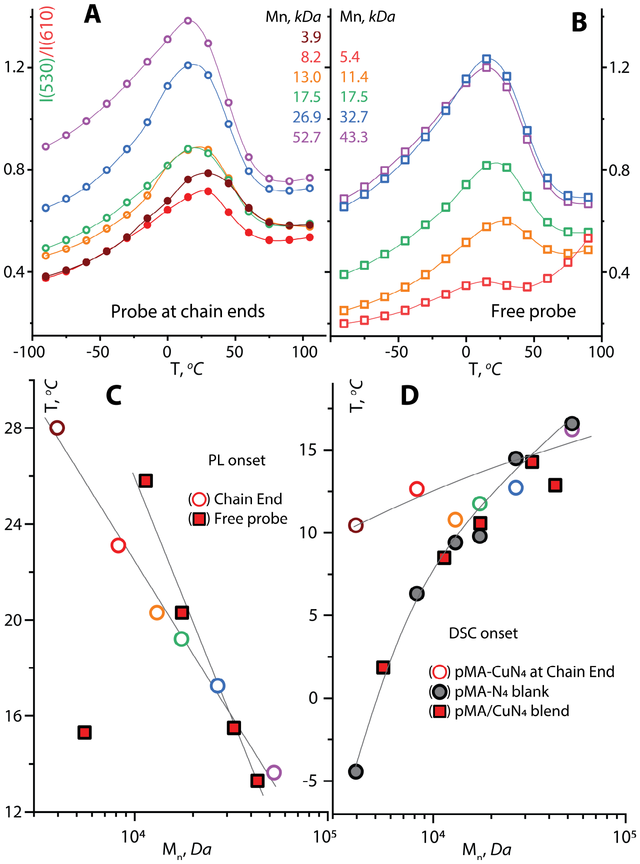

Figure 3. Ratiometry data for end labelled pMA samples (A) and pMA blends with freely dispersed CuN_4 probes (B); (C) M_n dependence of the probe mobilization onset temperature in these polymers; (D) DSC data for charged and neutral pMA samples and pMA/CuN4 blends indicating T_g perturbation; all lines to guide the eye.

Having observed that end group confinement in pMA is M_n dependent we expected similar differences in the probe mobilization dynamics. One would assume that reaching identical extent of probe mobility in a highly confined medium would require a higher temperature compared to the less confined packing. Indeed, analysis of the ratiometry data in Figure 3A points out that high M_n pMA permits chain end mobilization at significantly lower temperatures compared to low M_n pMA that has more confined chain end groups (Figure 3C). The onset of end-group mobilization in the pMA series varies from 28.0°C for the 3.9 kDa sample to 13.8°C for the 52.7 kDa sample with the latter value being similar to the bulk T_g measured using differential scanning calorimetry (DSC, Figure 3D). Notably the PL onset temperatures, reflective of a *local* T_g in the chain end vicinity, scale monotonically with *log(M_n)* pointing to two separate features of the local chain end behavior. Firstly, to the apparent lack of correlation with entanglement M_n,[34-35] and secondly, to a continuous nature of M_n dependence that contrasts the T_g saturation behavior implied by the Flory-Fox relations for the polymer bulk.

The differences we observed for local PL-based T_g also translate to the bulk of end-labelled pMA. The presence of a covalently linked large cationic Cu complex at the chain end perturbs the bulk T_g of these polymers (Figure 3D) that undergo glass transition at significantly higher temperature compared to their neutral counterparts (**pMA-N4** vs **pMA-CuN4**, Figure 1 and 3D). At largest, the differences reach ca. 15 degrees as in the case of 3.9 kDa sample and in line with previous reports,[20] they diminish upon increase of M_n when the chain end concentration decreases.

To check whether local and bulk T_g perturbations are correlated we prepared a sets of control pMA samples with probe molecules freely dispersed in the polymer. We expected that the free probe would be similarly capable of confining in pMA and demonstrate a local T_g trend similar to that of end-labelled samples. Indeed, the PL onset temperature for a free probe in pMA exhibits monotonic M_n dependence similar to that of the end labelled series (Figure 3B/C). The sole exception in this series is a low M_n sample where the FVE size might be too small to incorporate CuN_4 probe. At the same time, addition of a freely dispersed probe did not perturb the bulk T_g of pMA. The data plotted in Figure 3D is similar to the reference pMA series with neutral end groups. This suggests that FVE size, its occupancy and probe confinement are likely to impact the bulk T_g only if a bulky end-group is covalently linked to the polymer chain.

Seeking to rationalize the importance of M_n dependent confinement for the bulk behavior we note the consistency of this idea with theories suggesting that the glassy polymers can experience caging effects where the onset of glass transition is marked by the ability of polymer fragment to leave the cage formed by its nearest neighbors.[36] Similar analogies can be drawn with granular materials and macroscopic systems subject to jamming[37-39] that might be behind the strong T_g perturbations observed for end labeled pMA samples with the highest degree of end group confinement. Finally, it is known that the presence of end groups can significantly alter the diffusion rates as shown by Matsushita and co-workers[40] who analyzed diffusion rates in cyclic and linear polystyrenes. All the phenomena above can affect the polymer mobilization onset, thus affecting the bulk T_g in pMA series with covalently linked probe molecules.

Out data so far suggests that the ability of polymer of specific length to form voids and confine small molecules is a general behavior of a polymer governed by its M_n rather than being an artefact or consequence of probe incorporation. To verify this, we prepared a series of control samples by two- and tenfold dilution of the end-labelled pMA (8.2 kDa) with its neutral counterpart of similar M_n. We registered nearly identical ratiometric traces for these samples with PL onset temperatures for this dilution series similar within 1° despite probe concentrations varied tenfold (Figure S2.4). Additionally probe aggregation was ruled out using confocal lifetime imaging microscopy reporting no heterogeneities in **pMA-CuN4** (Figure S2.7-2.8 in the Supporting Information). Taken together this data suggests that end group confinement and resulting M_n dependence of the probe mobilization dynamics might be a purely structural phenomenon.

If this suggestion is correct, then the structure and placement of the probe molecule should dramatically alter the local PL data registered in pMA, especially in the case of significant size mismatch or disruption of probe confinement. We tested this using two sets of controls with the first series featuring CuN_4 probes attached randomly to the pMA chains. We observed no M_n dependence of the PL onset in this set of samples (Figure 4B and Figure S2.5 for ratiometry curves) confirming that the probe attached at random positions does not confine uniformly and remains insensitive to M_n variations. Similarly, such probe attachment does not increase the bulk T_g contrary to what was observed for the end-labelled pMA (Figure 4C).

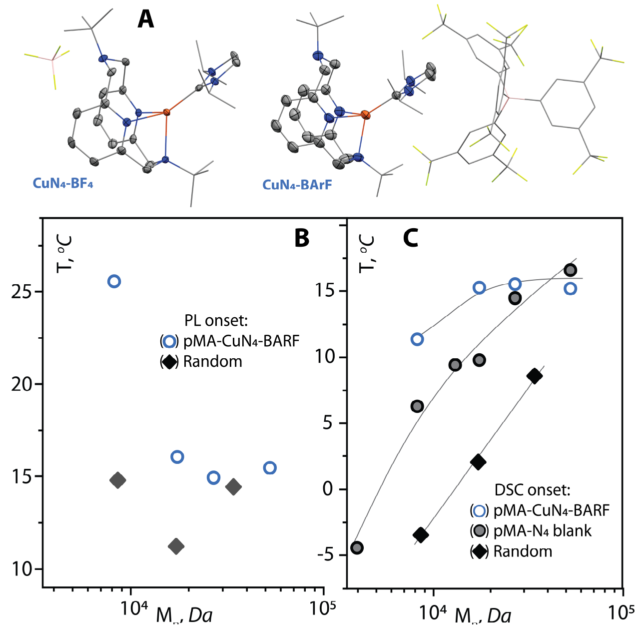

Figure 4. (A) Solid state structures of small molecule probes with tetrafluoroborate and BArF counterions indicating their different sizes, structures adopted from Refs. 29-30; (B) Comparison of PL data for end- and side chain labelled pMA; (C) DCS data for these polymers compared to the neutral pMA-N4 reference.

Since packing voids in pMA have a finite size, the second set of controls was prepared to induce a size mismatch between the luminescent probe and FVE. We used a large CuN_4-BARF probe (Figure 4A) that is ca 2nm in size – twice larger than CuN_4-BF_4 probe used throughout this work – a value exceeding pMA length of persistence.[34, 41] We found that the size mismatch induced by large probe renders pMA/CuN_4-BARF blends entirely unresponsive - no ratiometric response to glass transition was found in samples where the large probe was freely dispersed (Figure S2.6). This suggests that confinements capable of incorporating the probe are generated by the polymer host rather than probe-induced.

Interestingly, the large BARF probe that was unresponsive in feely dispersed form, becomes sensitive to glass transition once linked to the polymer end group covalently (Figure 4B and S2.3). Likely due to its disturbed confinement, the PL onset for this sample series is largely M_n independent. Due to its covalent attachment, the bulky BARF probe is capable of acting as diffusion constraint as it perturbs the bulk T_g by ca. 5 degrees similar to its smaller sized counterpart (Figure 4C).

Summarizing our observations we highlight two distinct phenomena revealed by the probe studies in pMA. Firstly, we find that pMA can apparently confine chain end groups and small emissive molecules dispersed in this polymer. The extent of confinement depends on molecular weight with low M_n glasses providing more compact confinements that imply smaller FVE sizes in low M_n polymers. We confirm that such confinement does not require covalent incorporation of the probe molecule but relies on the similarity between the probe size and that of FVE. Since the common end groups in synthetic polymers are smaller than CuN_4 we conclude that almost universally polymer end groups should experience these confinement effects.

We further show that end group size and structure are the likely causes of T_g perturbation observed in a number of previous reports.[20] Based on our probe placement studies we link this perturbation to the chain ends acting as diffusion constraints that are affected by confinement effects expressed strongly in low M_n glasses. This explains why low M_n glasses are particularly susceptible to T_g perturbations due to end group structure variations. Ironically, this line of reasoning suggests that the largest T_g perturbation would result in the weakest $\log(M_n)$ dependence of the T_g making this effect easy to overlook unless it is intentionally investigated.

Finally, we highlight the capacity of environmentally sensitive emissive probes like CuN_4 to reflect the multitude of environments found in a simple linear homopolymer. We show how placement chemistry dramatically affects the probe behavior that in some cases renders the probe entirely unresponsive. We anticipate that with more advanced probe designs it should be possible to assess the structural aspects of probe behavior in a quantitative way.

In conclusion we note that placing emissive molecules in polymer glasses is arguably a common practice in a variety of fields. Numerous light generation applications involve using polymer glasses as dye hosts and characterizing emission of new luminescent compounds in PS or PMMA films is a regular practice in materials science. It is not uncommon for luminescence in glasses to differ from that in solution or pristine solid. Our work suggests that complex structural phenomena may be driving these differences. Namely, we show that a polymer glass is a highly irregular solvation medium offering a variety of voids and environments for luminophore incorporation that make the common view on luminescent compounds being simply *dissolved* in a polymer glass no longer valid. On the other hand, selective and structure-guided incorporation of luminophores opens up a new tool for designing emissive glassy materials where confinement effects and PL environmental sensitivity can tune the material performance via the productive interplay disclosed in this work.

ASSOCIATED CONTENT

Supporting Information contains synthesis details and full characterization data. It is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

GAF kindly acknowledges Dr. Vera Gorelova of WUR for confocal microscopy studies and NWO for individual Veni grant.

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