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# Excess wing and Johari-Goldstein relaxation in binary mixtures of glass formers

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Dielectric loss spectra of pure quinaldine and tert-butylpyridine and their mixtures with tri-styrene are presented. The pure systems present an excess wing and no secondary peaks in the temperature interval from above to well below the glass transition. However, when mixed in low concentration with tri-styrene the excess wing is replaced by a distinct secondary peak. This distinct process can be identified as a Johari-Goldstein relaxation within the Coupling Model interpretation. In the frame of the Coupling Model the transition from the relaxation scenario with the excess wing to that with a distinct secondary peak is related to the increase of intermolecular constraints. In our case this increase of constraints is due to the low mobility component of the mixture (tri-styrene).

*Keywords:* Glass formers; mixture; excess wing; Johari Goldstein relaxation; nearly constant loss

*AMS Subject Classification:*

## Introduction

The hypothesis of a two step relaxation dynamics (for example see Ref. [1-3] and references therein), and the recent investigations about the origin of secondary relaxation in for glass formers [4-12] raised the question whether the secondary process is an universal feature of the relaxation dynamics. Experimentally, more than one secondary process can be observed in some glass formers with complex molecular structure [6,9,10]. Two main mechanisms for the secondary processes are generally proposed: an intramolecular motion of some molecular subgroup dynamically decoupled from the rest of the molecule [13], or a small angle motion of the entire molecule as a whole [3,5]. The process originating from the last mechanism is usually referred as Johari Goldstein (JG) process, and it is supposed to reflect an universal relaxation mechanism. However, loss spectra of some glass formers show no evidence of any secondary peak, but only an extra loss contribution (excess wing, EW) in the high frequency tail of the structural process. Such a contribution appears as a power law with exponent smaller than that characterizing the high frequency part of the structural peak. The microscopic origin of the EW was debated and it was discussed whether it is a secondary peak submerged by the structural or it is a relaxation feature connected to the structural process [16-27]. In some cases the appearance of the EW is only a matter of a reduced frequency or temperature interval of investigation: by extending them it is observed that the EW becomes a secondary peak separated from the structural one [14,15,21]. However, these are particular cases

that cannot be confused with those where the EW is detected even measuring over a wide frequency interval in the deep glassy state.

Some articles discussed the origin of the EW proposing different interpretations. Early approaches interpreted the EW in the frame of the mode coupling theory, but without success [16], or, on the basis of scaling arguments, as an inherent part of the  $\alpha$ -relaxation [17,18]. A new approach to the EW in term of the MCT was recently proposed [19] but not verified on the available data. Kudlik and co-authors [20] suggested that supercooled liquids can be classified in two classes, depending if in the glassy state they show to an EW or a  $\beta$ -relaxation mechanism. Later on, different experimental results have cast doubts on the validity of this classification [22,23]. Schneider and co-workers observed the EW of glycerol and propylene carbonate transforming into a secondary peak after aging at temperatures below  $T_g$  [26]. They explained such behaviour suggesting that different dependence on aging of the structural and secondary peaks favours the observation of the latter. Similarly, dielectric spectra of the trimer of propylene glycol at high pressure showed an EW that, after aging below  $T_g$ , transformed into a shoulder [25]. Dielectric measurements on a family of polyalcohols and polymers showed that the secondary relaxation peak gets close to the structural with decreasing the number of repeating units, until it merges forming an EW [12,27,28]. The application of very high pressure transform the EW of threitol and glycerol into a partially merged secondary peak [27]. Finally, in three cases the EW was changed into a secondary peak after mixing a polar glass former with one having a negligible dielectric signal (picoline in o-terphenyl, picoline in tri-styrene, and propylene carbonate in poly(methyl methacrylate)) [22-24].

In the case of polyalcohols and oligomers the appearance of a secondary peak at large number of repeating units was explained in terms of increase of the effects of the many molecules dynamics and intermolecular coupling [4]. This explanation was quantitatively inspired by the Coupling Model (CM) [3] predicting that the frequency separation of structural and secondary Johari-Goldstein, JG, peaks is strictly related to the coupling parameter ( $n$ ),

$$n = \left[ \log(\tau_{\alpha, \max}) - \log(\tau_{JG}) \right] / \left[ \log(\tau_{\alpha, \max}) + 11.7 \right] \quad (1)$$

where  $\tau_{\alpha, \max} = 1/(2\pi\nu_{\alpha, \max})$  and  $\tau_{JG, \max} = 1/(2\pi\nu_{JG})$  are the relaxation times corresponding to the maximum frequency  $\nu_{\alpha, \max}$  and  $\nu_{JG}$  of the structural and JG peaks, respectively. The coupling parameter, which is related to the stretching of the Kohlrausch Williams Watts (KWW) function used to fit the structural peak,  $n = 1 - \beta_{KWW}$ , is usually considered a measure of the intermolecular coupling. The greater is the value of  $n$  the greater is the effect of the intermolecular constraints leading to the many molecules dynamics. According to Eq. (1) for a fixed value of  $\tau_{\alpha, \max}$  (or  $\nu_{\alpha, \max}$ ) the separation of the JG peak must be larger for greater values of  $n$ . In both polyalcohols and oligomers, for larger number of repeating units a larger value of  $n$  was observed and accordingly a secondary peak separated from the structural [4,12,28-29]. Instead, for short oligomers a smaller value of  $n$  was found and the secondary peak was replaced by an EW. The same explanation was recently [30] successfully used to interpret the appearance of a secondary peak in mixtures of o-terphenyl in tri-styrene and picoline in tri-styrene. Consistently the scenario can be explained considering that the EW is a secondary peak of the JG type [4], which for small enough values of  $n$  is so close to the structural peak that it results submerged by it.

In this work we extended previous investigations considering the secondary dynamics of two pure systems, presenting excess wing, and their mixtures with a non-polar compound. In this latter case the EW was replaced by a secondary peak. We evidenced the role of intermolecular interactions in defining the two relaxation scenario and we interpreted the emerged secondary peak as a JG relaxation in term of the CM.

## Experiment

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3 Tert-butylpyridine (TBP, molecular weight 135.21g/mol), quinaldine (Qn, molecular weight  
4 143.19g/mol), and tri-styrene (3Styr, molecular weight 370 g/mol, polydispersity 1) were bought  
5 from Aldrich, Fluka and PSS, respectively and used as received. TBP and Qn are quite rigid polar  
6 molecules (inset of Fig. 1); in both cases the dipole moment arises from the nitrogen atom  
7 substituting a carbon inside the aromatic ring, but due to the different molecular structure the values  
8 are different: for TBP it is about 2.7 Debye and for Qn about 3.8 Debye. Instead, 3Styr is an  
9 oligomer of the styrene with three repeating units, and it is much less polar than the formers having  
10 a molecular dipole moment of 0.2 D. The glass transition temperature of tri-styrene is 233 K as  
11 determined by dielectric spectroscopy differential scanning calorimetry.

12 Dielectric spectroscopy measurements were performed in the frequency interval  $10^{-2}$  Hz -10 MHz,  
13 using the Novocontrol Alpha Analyzer. A parallel plate capacitor separated by sapphire spacer  
14 (empty capacity  $\sim 60$  pF) was used as sample cell. The configuration of the cell is similar to that  
15 used in Ref. [8], with the distance between the electrodes kept constant within 0.4% over the  
16 investigated temperature range. The temperature of the sample was controlled by a conditioned  
17 nitrogen flow. Dielectric spectra were measured isothermally, after stabilizing the temperature  
18 within 0.1 K for 1 hour. For measurements below  $T_g$ , the sample was cooled to the final temperature  
19 with a cooling rate of about 0.05 K/min. Differential scanning calorimetry was performed for each  
20 mixture and revealed a single  $T_g$  indicating that no phase separation nor crystallization was present.  
21 Calorimetric data will be presented in a further paper [31].  
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## 28 Results and Discussion

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31 Dielectric loss spectra (Fig. 1) of TBP and Qn above  $T_g$  show the conductivity contribution, due to  
32 the ionic impurity, appearing as a rise of the signal at low frequencies (for clarity the contribution is  
33 shown only for few spectra in Fig. 1), and the contribution due the structural relaxation dynamics,  
34 appearing as a peak. These two processes slow down with temperature, and finally below  $T_g$  also  
35 the structural peak disappears from the investigated frequency window. On the high frequency we  
36 observe an excess loss contribution, appearing above  $T_g$  as a deviation from the one side Fourier  
37 Transform of the KWW function fitting the structural peak (see continuous lines in Fig.1). In Fig. 1  
38 the power law describing the excess wing is evidenced in the loss spectra of TBP and Qn measured  
39 at 169 K and 188 K, respectively. The exponents of the power laws are  $-0.29 \pm 0.01$  and  $-0.40 \pm 0.01$ ,  
40 respectively, both smaller than those characterising the high frequency tail of the structural peak as  
41 determined from the KWW fit. This difference make it possible to distinguish between the excess  
42 wing and the common power law characterizing the high frequency tail of the structural peak.  
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45 The excess wing in both samples moves towards lower frequency with the structural peak and  
46 disappears from the investigated frequency window well below  $T_g$  (Fig. 1). In this region the loss  
47 spectra evidence a weak decrease with frequency; such loss contribution is well studied in ionic  
48 conductors and it is usually called nearly constant loss [32,33]. This behaviour can be reasonably  
49 fitted by a second power law whose exponent decreases with temperature (Fig. 1). For Qn the  
50 exponent decreases from  $-0.21 \pm 0.01$  at 143 K to  $0.15 \pm 0.01$  at 113 K, and in TBP from  $0.12 \pm 0.01$   
51 at 163 K to  $0.11 \pm 0.01$  at 133 K. It is worth to note that a similar phenomenology was reported in Ref.  
52 [3] for few other glass forming systems, namely propylene carbonate, glycerol, cresolphthalein-  
53 dimethyl ether and N-methyl- $\epsilon$ -caprolactam. Our results on the pure TBP and Qn confirm and  
54 extend those reported in previous works in two points. First of all, we confirm that the excess wing  
55 is a relaxation feature characteristic of systems with a narrow structural peak. The coupling  
56 parameter, which is a measure of the deviation of the structural peak from the Debye relaxation, is  
57  $0.30 \pm 0.03$  for Qn and  $0.37 \pm 0.02$  for TBP (Fig. 2), which compares with  $n=0.29$  of Glycerol and  
58 other systems showing EW, as it was already discussed in other publications, for example [4,30].  
59 The second important result is that in system with EW below  $T_g$  it is possible to observe a weak  
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3 frequency dependence of dielectric loss, which cannot ascribed to the extrapolation of the high  
4 frequency tail of the structural peak or to the extrapolation of the EW.

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6 The main goal of our work is the investigation of the relaxation mechanism at the basis of the EW.  
7 To extend the results of previous papers [12,23,24,30], we investigated the possibility to transform  
8 the EW into a secondary peak by changing intermolecular coupling among the investigated  
9 molecules. In our work we changed intermolecular coupling by mixing the polar TBP and Qn with  
10 3Styr. The dipole moment of the former molecules is more than a factor 10 greater than that of  
11 3Styr, so that we can expect the a ratio of more than 2 orders of magnitude between the dielectric  
12 strength of the relaxations. The difference in the intensity of the signals assures that dielectric  
13 response of the mixture reflects the relaxation dynamics of TBP and Qn molecules dispersed in the  
14 3Styr matrix, and no direct contribution of 3Styr molecules is observed.

15  
16 Dielectric spectra of pure Qn and TBP present a narrower structural relaxation compared to that of  
17 their mixtures with 3Styr (Fig. 2). The coupling parameter changes from  $n=0.37$  to  $0.55$  (from pure  
18 Qn to the mixture with Qn weight ratio of 5%) and from  $n=0.30$  to  $0.58$  (from pure TBP to the  
19 mixture with TBP weight ratio of 16%). It is common that the structural peak in mixtures with  
20 similar percentages of the two components is broader than those of the pure systems. In such cases  
21 the broadening is attributed to the effect of local composition heterogeneities, usually named as  
22 concentration fluctuations [34]. Instead, in the limit of high dilution (concentration less than 1%)  
23 the broadness of the observed structural peak can vary between that of the pure host system, and  
24 that of a Debye function [35] mainly depending on the relative mobility of the molecules. In the  
25 case of low, but not dilute, concentration of a polar component with an apolar one characterized by  
26 lower mobility, as in our mixtures, the concentration fluctuations contribution should be negligible,  
27 but a certain broadening is observed. The origin of the latter was ascribed to the larger effects of  
28 dynamic constraints imposed to the polar molecules from the slower molecules of the apolar  
29 component. This effect was related to the separation between structural and JG secondary peak [30].  
30 The CM predicts that the frequency separation between the JG secondary and the structural peaks is  
31 larger for systems with greater dynamic heterogeneity, i.e. larger value of coupling parameter (Eq.  
32 1). In a neat system a good estimation of dynamic heterogeneity is the value of  $n$  determined from  
33 the broadness of the structural peak. Usually in mixtures such estimation is not reliable especially  
34 when concentration fluctuations is important, whose effects lead to a broadening of the structural  
35 peak reflecting only statistic and not dynamic effects. A discussion of this topic together with a  
36 detailed presentation of the extension of the CM to bi-component mixtures is in Ref. [30]. In our  
37 case fluctuations concentration can be neglected due to the low concentration of the polar  
38 component: actually one polar molecule is surrounded mainly by styrene repeating units and a  
39 concentration fluctuations cannot significantly change this environment. Our data confirm that a  
40 broadening of the structural peak, due to an increase of many molecules interactions, leads to a  
41 greater separation between secondary JG relaxation and structural peak, as discussed in [30]. In  
42 fact, in both pure systems, with narrow structural peak, only the EW is present, whereas in the  
43 mixtures, presenting a broader structural peak, a well separated secondary peak appears. The new  
44 peak is sensitive to temperature and the activation energy estimated below  $T_g$  is  $54\pm 1$  kJ/mol for the  
45 Qn mixture and  $29\pm 1$  kJ/mol for the TBP mixture.

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47 The interpretation here proposed consider the EW as a hidden secondary relaxation. Such  
48 hypothesis can be quantitatively confirmed in term of the CM. In fact, Eq. (1) can be rewritten as  
49  $v_{JG}=(2\pi t_c)^{-n}v_\alpha^{(1-n)}$ , where  $t_c=2$  ps, which allows to calculate the position of the JG relaxation once  
50 the values of  $v_\alpha$  and  $n$  are known [3,4]. The calculated values of  $v_{JG}$  are in fair agreement with those  
51 of the observed secondary peaks in both mixtures (vertical arrows in Fig. (2)). In the case of the  
52 pure system the JG relaxation is predicted in the region of the EW, hidden beneath the structural  
53 peak. The CM suggests as relaxation mechanism a continuous evolution from a local restricted  
54 relaxation process of the whole molecules (JG) to a cooperative relaxation (structural process) [3,4].  
55 Both the excess wing and the secondary process emerging in the neat system and mixture,  
56 respectively, reflect the restricted and non cooperative motion of the whole molecule.

## Conclusion

Dielectric loss spectra of pure quinaldine and tert-butylpyridine and their mixtures with tri-styrene are presented. The pure systems present an excess wing and no secondary peak, whereas the mixtures with tri-styrene show a distinct secondary peak. In the frame of the Coupling Model the transition from the relaxation scenario with excess wing to that with secondary peak is related to the increase of intermolecular constraints induced by the low mobility component of the mixture (tri-styrene). The secondary peak observed in the mixture can be interpreted as Johari-Goldstein.

## References

- [1] W. Götze, M. Sperl Phys. Rev. Lett. **92**, 105701 (2004).
- [2] H. Tanaka J. Non-Cryst. Solids **351**, 3396 (2005); H. Tanaka J. Non-Cryst. Solids **351**, 3385 (2005).
- [3] K.L. Ngai, M. Paluch J. Phys. Chem. B, **107**, 6865 (2003); K.L. Ngai J. Phys.: Condens. Matter **15**, S1107 (2003).
- [4] K.L. Ngai, M. Paluch J. Chem. Phys. **120**, 857 (2004).
- [5] M. Vogel, C. Tschirwitz, G. Schneider, C. Koplin, P. Medick, E. Rössler J. Non-Cryst. Solids **307-310**, 326 (2002).
- [6] D. Prevosto, S. Capaccioli, M. Lucchesi, P.A. Rolla and K.L. Ngai J. Chem. Phys. **120**, 4808 (2004).
- [7] N.B. Olsen, T. Christensen, J.C. Dyre, Phys. Rev. E **62**, 4435 (2000).
- [8] H. Wagner, R. Richert, J. Phys. Chem. B **103**, 4071 (1999).
- [9] M. Paluch, S. Pawlus, S. Hensel-Bielowka, E. Kaminska, D. Prevosto, S. Capaccioli, P. A. Rolla, K.L. Ngai, J. Chem. Phys. **122**, 234506 (2005).
- [10] D. Pisignano, S. Capaccioli, R. Casalini, M. Lucchesi, P.A. Rolla, A. Justl, E. Rössler J. Phys.: Condens. Matter **13**, 4405 (2001).
- [11] S. Hensel-Bielowka, M. Paluch, Phys. Rev. Lett., **89**, 025704 (2002).
- [12] J. Mattsson, R. Bergman, P. Jacobsson, L. Börjesson Phys. Rev. Lett., **90**, 075702 (2003).
- [13] N.G. McCrum, B.E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids* (Wiley, New York, 1967).
- [14] M.T. Viciosa, C.M. Rodriguez, M. Dionisio J. Non-Cryst. Solids **351**, 14 (2005).
- [15] S. Maslanka, M. Paluch, W.W. Sulkowski, C.M. Roland J. Chem. Phys. **122**, 084511 (2005)
- [16] A. Hoffmann, F. Kremer, E. W. Fischer, and A. Schönhals, in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer, Berlin, 1994), p. 309.
- [17] P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Carini, Phys. Rev. Lett. **65**, 1108 (1990).
- [18] R. V. Chamberlin, Phys. Rev. B **48**, 15 638 (1993).
- [19] H.Z. Cummins J. Phys.: Condens. Matter **17**, 1457 (2005).
- [20] A. Kudlik, S. Benkhof, T. Blochowicz, T. Tschirwitz, E.A. Rössler J. Mol. Struct. **479**, 201 (1999).
- [21] S. Capaccioli, D. Prevosto, M. Lucchesi, P.A. Rolla, R. Casalini, K.L. Ngai J. Non-Cryst. Solids **351**, 2643 (2005).
- [22] T. Blochowicz, E.A. Rössler, Phys. Rev. Lett. **92**, 225701 (2004).
- [23] T. Blochowicz, *Broadband Dielectric Spectroscopy in Neat and Binary Molecular Glass Formers*; ISBN 3-8325-0320-X, Logos Verlag:Berlin, 2003.
- [24] C. Svamberg, R. Bergman, P. Jacobsson Europhys. Lett. **64**, 358 (2003).
- [25] R. Casalini, C. M. Roland, Phys. Rev. Lett. **91**, 015702 (2003).
- [26] U. Schneider, R. Brand, P. Lunkenheimer, A. Loidl Phys. Rev. Lett. **84**, 5560 (2000).
- [27] S. Hensel-Bielowka, S. Pawlus, C.M. Roland, J. Ziolo, M. Paluch Phys. Rev. E **69**, 050501 (2004).

- [28] C. Leon, K.L. Ngai, C.M. Roland J. Chem. Phys., **110**, 11585 (1999).  
 [29] A. Doss, M. Paluch, H. Sillescu, G. Hinze Phys. Rev. Lett., **88**, 095701 (2002).  
 [30] S. Capaccioli, K.L. Ngai J. Phys. Chem. B, **109**, 9727 (2005).  
 [31] K. Kessairi, S. Capaccioli, *et al.* in preparation.  
 [32] K.L. Ngai, C. Leon Phys. Rev. B **66**, 064308 (2002).  
 [33] R. Casalini, K.L. Ngai J. Non-Cryst. Solids **293-295**, 318 (2001).  
 [34] R. Kant, S. K. Kumar, Macromolecules **36**, 10087 (2003).  
 [35] W. Huang, R. Richert J. Chem Phys. **124**, 164510 (2005).

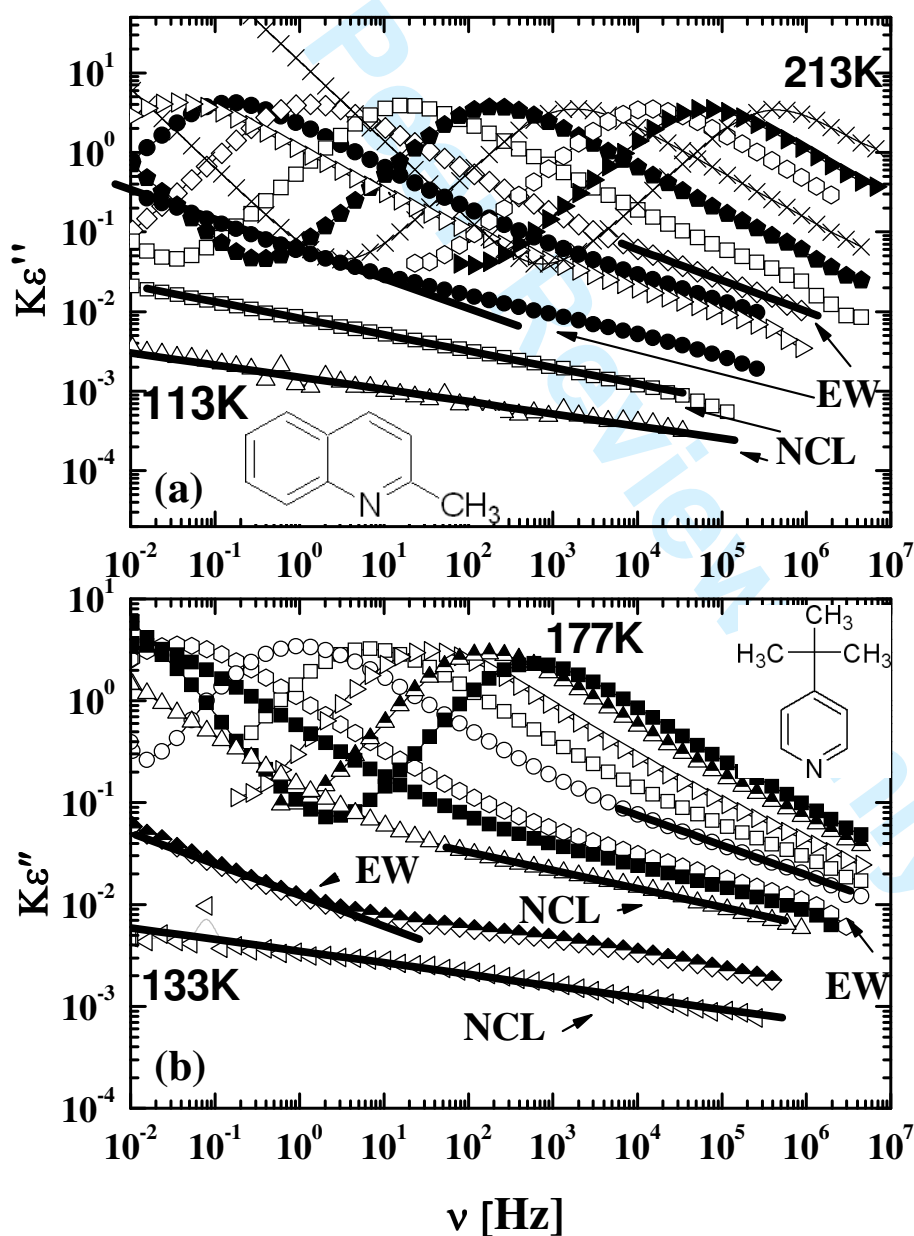




Fig.1. (a) Double logarithmic representation of dielectric loss spectra of Quinaldine at the temperatures (from the right to the left) 213, 208, 204, 200, 196, 192, 188, 185, 183, 173, 143, 113 K. The EW contribution is evidenced in the spectra at 188 and 143 K, whereas the NCL is evidenced in the spectra at 173 and 113 K. In the inset the molecular structure is reported. (b) Double logarithmic representation of dielectric loss spectra of Tert-butylpyridine at the temperature (from the right to the left) 177, 175, 173, 171, 169, 166, 165, 163, 158, 133 K. The EW contribution is evidenced in the spectra at 169 and 158 K, whereas the NCL is evidenced in the spectra at 163 and 133 K. In the inset the molecular structure is reported.

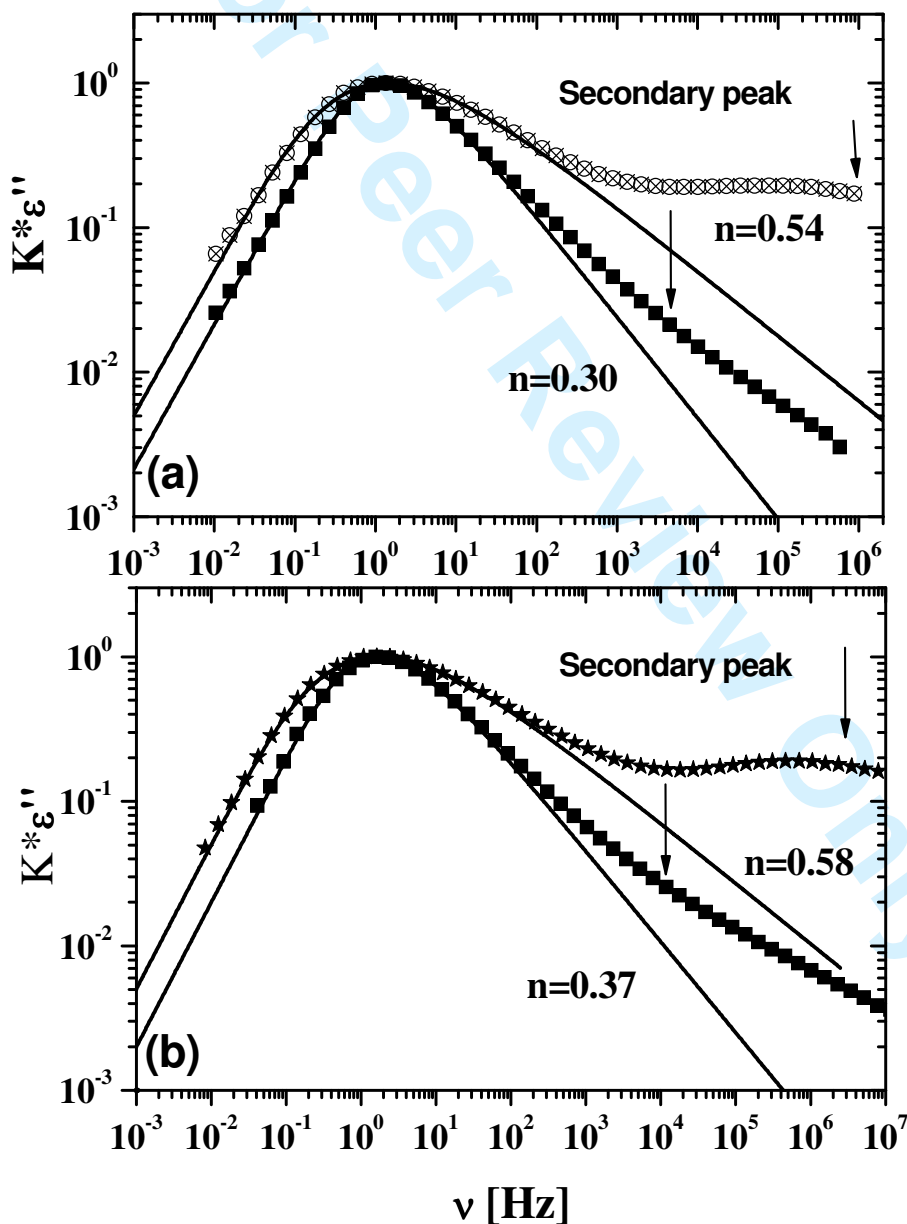


Fig. 2 Normalized loss spectra of pure (a) Qn (squares, 188 K) and mixture of 5% Qn in 3Styr (crossed open circles, 236 K) and (b) pure TBP (squares, 169 K) and mixture of 16% TBP in 3Styr (stars, 223 K). Each couple of spectra were measured so that the frequency of structural peak is

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3 nearly the same. When necessary a small horizontal shift factor was applied to obtain an exact  
4 match of the maxima. In both panels the continuous curves represent KWW curves to fit the  
5 structural peak, with reported values of the coupling parameters,  $n=1-\beta_{\text{KWW}}$ . The vertical arrows  
6 indicate the position of the JG secondary relaxation predicted by the coupling model.  
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