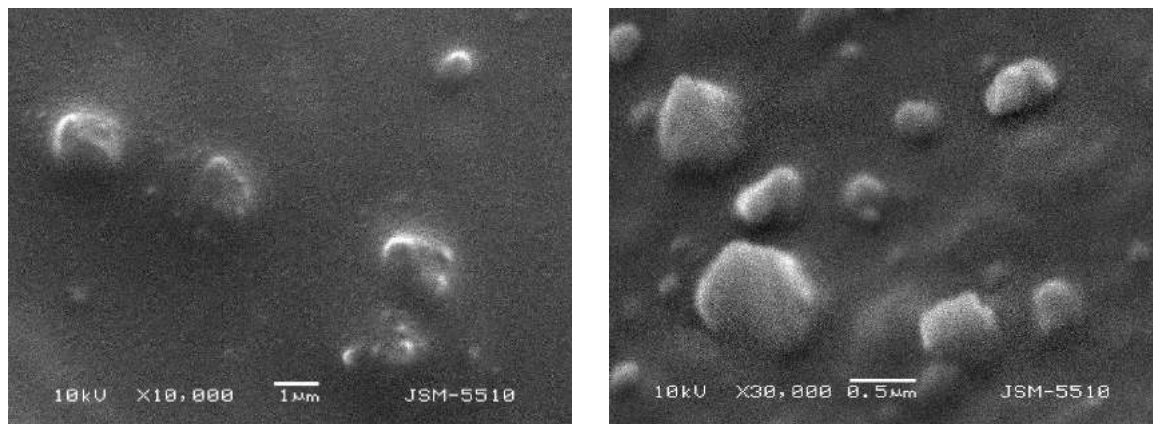


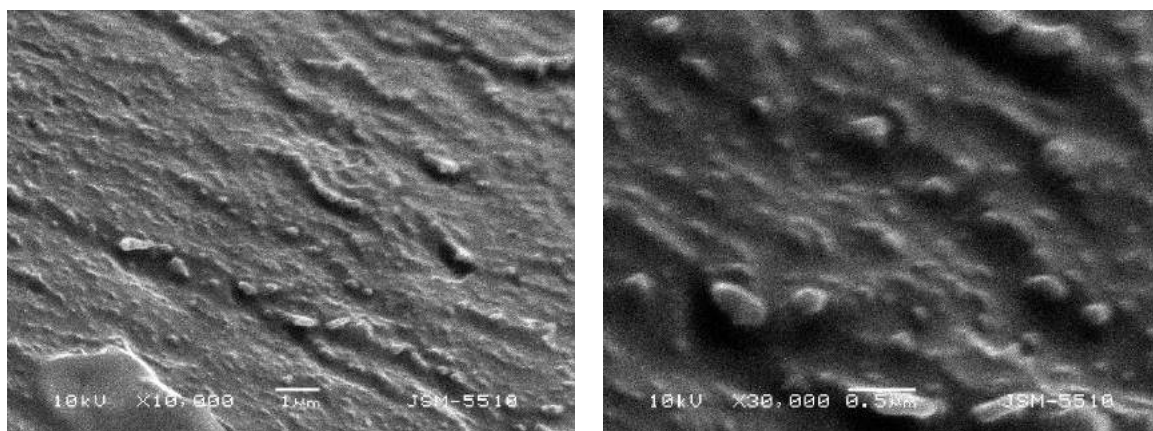
**Figure S1.** Chemical formulas of both monomers as well as of the drug used within the work.

*Characterization of IPN PMAA/PAAm both neat and loaded with VPM*

*Morphology*



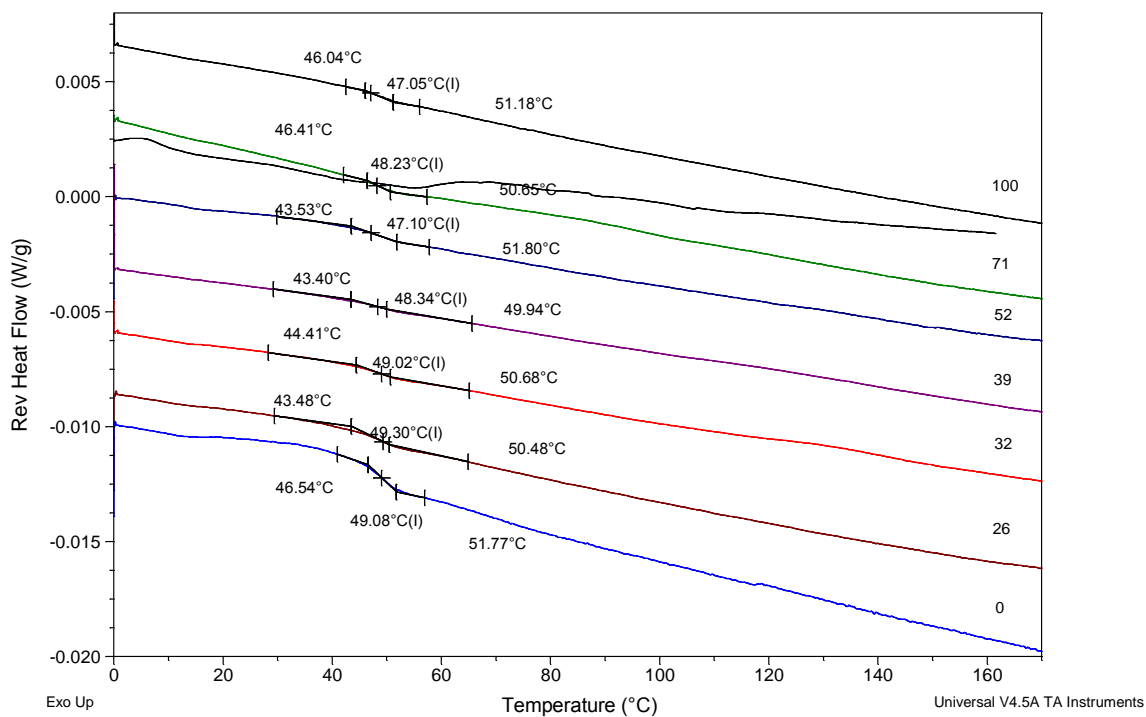
IPMA3 ( $\phi^{\text{PMAA}} = 0.52$ )



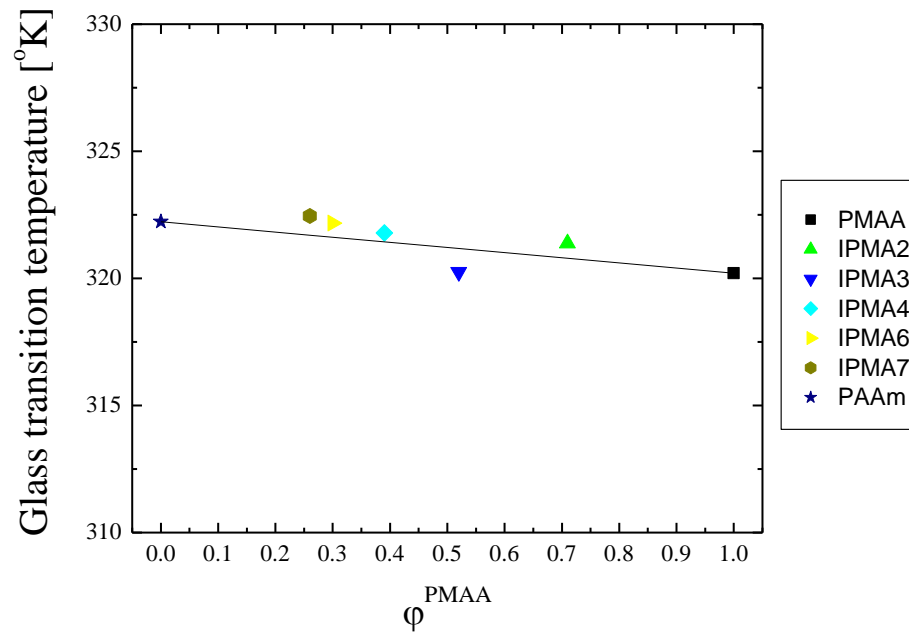
IPMA2 ( $\phi^{\text{PMAA}} = 0.71$ )

**Figure S2.** Morphology of the broken surfaces of two IPN PMAA/PAAm with different composition after loading with VPM.

### Thermal properties

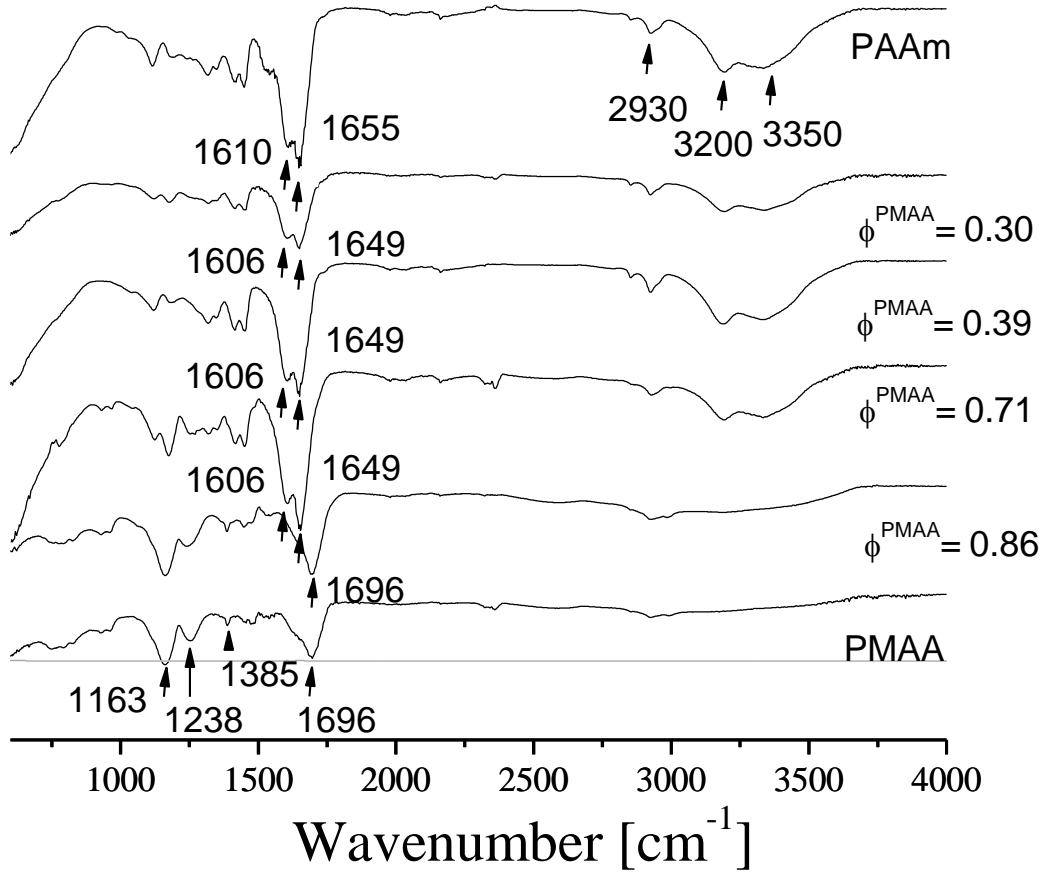


**Figure S3.** Reversing heat flow curves obtained by TM-DSC for PMAA/PAAm IPN and the respective SNs from PMAA and PAAm.



**Figure S4.**  $T_g$  dependence on IPN's PMAA/PAAm composition (line is drawn according to the additivity law).

ATR-IR Spectroscopy



**Figure S5.** ATR-IR spectra of IPN PMAA/PAAm and both SNs PMAA and PAAm.

**Table S1.** IR characteristic bands for both SNs PMAA and PAAm.

IR band	Attribution	Remarks
<b>PAAm</b>		
3350 $\text{cm}^{-1}$	$\nu^{\text{a}}_{\text{N-H}}$	intense and wide
3200 $\text{cm}^{-1}$	$\nu^{\text{s}}_{\text{N-H}}$	intense and wide
2930 $\text{cm}^{-1}$	$\nu^{\text{s}}_{\text{CH}_2}$	medium weak
1655 $\text{cm}^{-1}$	$\nu_{\text{C=O}}$ Amide I	very intense
1610 $\text{cm}^{-1}$	$\delta_{\text{N-H}}$ Amide II	a bend on the tail of Amide I
600-700 $\text{cm}^{-1}$	$\gamma_{\text{N-H}} + \gamma_{\text{CO}}$	intense, wide, complex (shoulder as the band starts at 500 $\text{cm}^{-1}$ )
<b>PMAA</b>		
1696 $\text{cm}^{-1}$	$\nu_{\text{C=O}}$	C=O stretching in carboxylic group of PMAA
1385 $\text{cm}^{-1}$	$\delta^{\text{s}}_{\text{CH}_3}$ of C-CH <sub>3</sub>	weak
1163, 1238 $\text{cm}^{-1}$	$\nu_{\text{C-O}} + \delta_{\text{OH}}$	intensive and wide

In Figure S4 are presented the IR spectra of PMAA/PAAm IPN with several different compositions along with the spectra of both SNs PMAA and PAAm. Table S1 summarizes the specific IR bands for both SNs, respectively for CONH<sub>2</sub> (PAAm) and COOH groups (PMAA). These bands change for the IPN. The wavenumber of the C=O stretching in the amide group (PAAm) decreased for all IPN from 1655 to 1649 cm<sup>-1</sup>. So does the band at ~1610 attributed to  $\delta_{N-H}$  Amide II - it decreased to 1606 cm<sup>-1</sup> for all IPN (Figure S4). The observed shift of both amide group originating bands to lower wavenumbers (which exceeds the instrumental resolution of ~ 2 cm<sup>-1</sup>) means that the amide group of PAAm interacts in the IPN with the COOH group from the PMAA.

The carboxylic groups of PMAA as expected also take part in the hydrogen bonds formation with amide groups of PAAm which is illustrated by the disappearing of the doublet at ~1161 cm<sup>-1</sup> and ~1236 cm<sup>-1</sup> (for  $\nu_{C-O} + \delta_{O-H}$ ) in the IPN as compared to the neat PMAA. Moreover, the C=O stretching of the PMAA carboxylic group appearing at ~1696 cm<sup>-1</sup> in the SN PMAA (Figure S4, Table S1) is obscured by the PAAm's amide bands at 1655 cm<sup>-1</sup> and 1610 cm<sup>-1</sup> in the IPN's spectra. That is most probably due to its shifting towards lower wavenumbers in the IPN as compared to the neat PMAA, which shifting originates from the participation of the respective group (C=O) in hydrogen bonds.

The characteristic VPM's bands are presented in Table S2. The VPM's N-H stretching vibration band at ~ 2800 – 2300 cm<sup>-1</sup> disappears in IPMA1 loaded with VPM which could be due to the formation of R<sub>3</sub>NH<sup>+</sup>:COO<sup>-</sup> ion pair, i.e. to the significant microenvironment change of the protonated amine group of VPM when loaded into the IPN caused by its interaction with COO<sup>-</sup> from PMAA. This result confirms the proposed at the beginning of the current work ionic interaction polymer vehicle-cationic drug, indirectly proved also by the DSC results (VPM amorphization).

The C-H stretching vibrations of the methoxy groups in VPM, which appear at ~2841 cm<sup>-1</sup> in the neat VPM, are shifted to 2838 cm<sup>-1</sup> in IPMA1, loaded with VPM, which is also an indication for drug-polymer interaction. The same interaction is the reason for the slight decrease in the wavenumber of the C=N stretching vibrations of the saturated alkyl nitrile in the neat VPM (~2237 cm<sup>-1</sup>) which appears at ~2235 cm<sup>-1</sup> in the IPMA1.

The changes in the peak shape (Figure 6) and the bands positions (Table S2) for the stretching vibrations of the  $-\text{OCH}_3$  group and  $-\text{C}\equiv\text{N}$  group of VPM most probably arise from the strong hydrogen bonding between VPM and the polymer matrix.

**Table S2.** IR characteristic bands for the neat drug VPM as compared to the same bands appearing in the IPMA1, loaded with VPM.

<b>VPM</b> [ <sup>20</sup> , <sup>21</sup> ]	2841 cm <sup>-1</sup>	2800 – 2300 cm <sup>-1</sup>	2237 cm <sup>-1</sup>	1593 cm <sup>-1</sup>	1516 cm <sup>-1</sup>	1462 cm <sup>-1</sup>	1257 cm <sup>-1</sup>
<b>IPMA1+VPM</b>	2838 cm <sup>-1</sup>	-	2235 cm <sup>-1</sup>	1591 cm <sup>-1</sup>	1516 cm <sup>-1</sup>	1458 cm <sup>-1</sup>	1257 cm <sup>-1</sup>
<b>Attribution</b>	C-H stretching vibrations of methoxy groups	N–H stretching vibrations of protonated amine	C=N stretching vibrations of saturated alkyl nitrile	C-H stretch of benzene ring	C-H stretch of benzene ring	C-H stretch of benzene ring	strong CO stretching vibrations of aromatic ethers
<b>Observed change</b>	slight decrease due to interaction with IPN matrix	disappear in the IPMA1, loaded with VPM, due to ionic interaction with IPN matrix	slight decrease due to interaction with IPN matrix	slight decrease due to possible interaction with IPN matrix	no change	slight decrease due to possible interaction with IPN matrix	no change

<sup>20</sup> J. Sahoo, P. N. Murthy, S. Biswal, Manik AAPS PharmSciTech, Vol. 10, No. 1, March 2009 (2009) 27-33

<sup>21</sup> B. W. Tekade, V. M. Thakare, U. T. Jadhao, F. Kazi The Pharm. Innov. J. 3 (2014) 48



