

NATURAL HETEROPOLYSACCHARIDE XANTHAN WITH NANOGEL PARTICLES AS THE BASIS FOR SYNTHESIS OF NEW POLYMER HYBRIDS



Zheltonozhskaya T.B.¹, Vretic L.O.², Tovstenko-Zabelin M.S.², Permyakova N.M.¹, Klepko V.¹, Klymchuk D.³

¹ Department of Polymer Physics, Institute of Macromolecular Chemistry of the NAS of Ukraine, 48 Kharkivske Shosse, Kyiv-02160, Ukraine.

E-mail: zheltonozhskaya@ukr.net

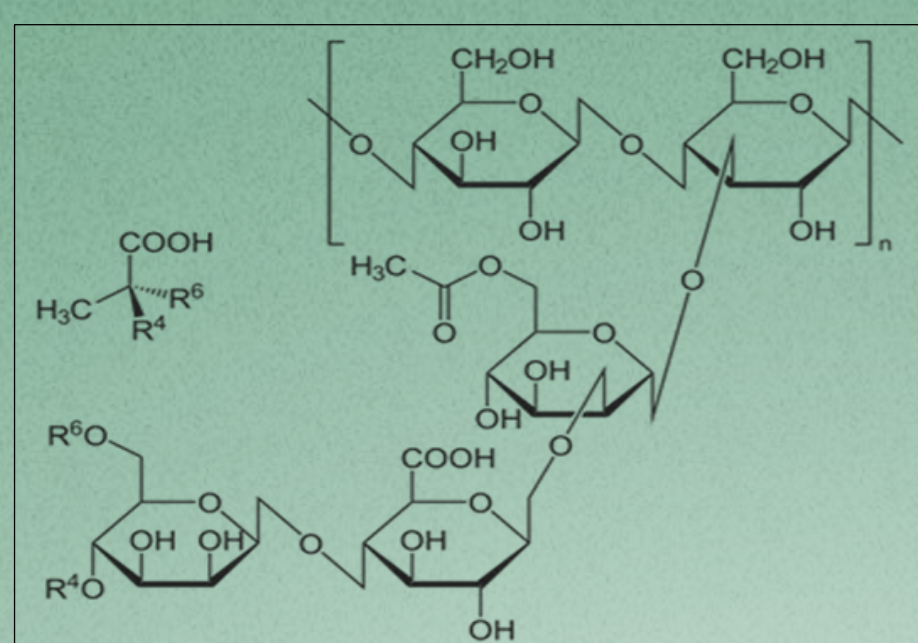
² Faculty of Chemistry, Taras Shevchenko National University of Kyiv, 60 Volodymyrska St., Kyiv- 01033, Ukraine.

³ M.G. Kholodny Institute of Botany of the NAS of Ukraine, 2 Tereshchenkivska St., Kyiv-01601, Ukraine.

Xanthan gum of microbial origin is currently considered one of the most interesting, studied and widely used natural polysaccharides due to its remarkable biocompatibility, biodegradability and non-toxicity. Having a regularly branched chemical structure and a negative charge in the side chains, its macromolecules can take both an elongated (helical) and a coiled conformation in solutions, depending on the balance of intra- and intermolecular electrostatic interactions and hydrogen bonds. **Xanthan** coils in aqueous solutions are physical nanogels with a micelle-like structure, which can be used to create new hybrid materials of the type: **nanogel "core" – polymer "corona"**. This work presents the implementation of this idea to obtain new **Xanthan/poly-N-isopropylacrylamide (X-g-PIPAAm)** hybrids.

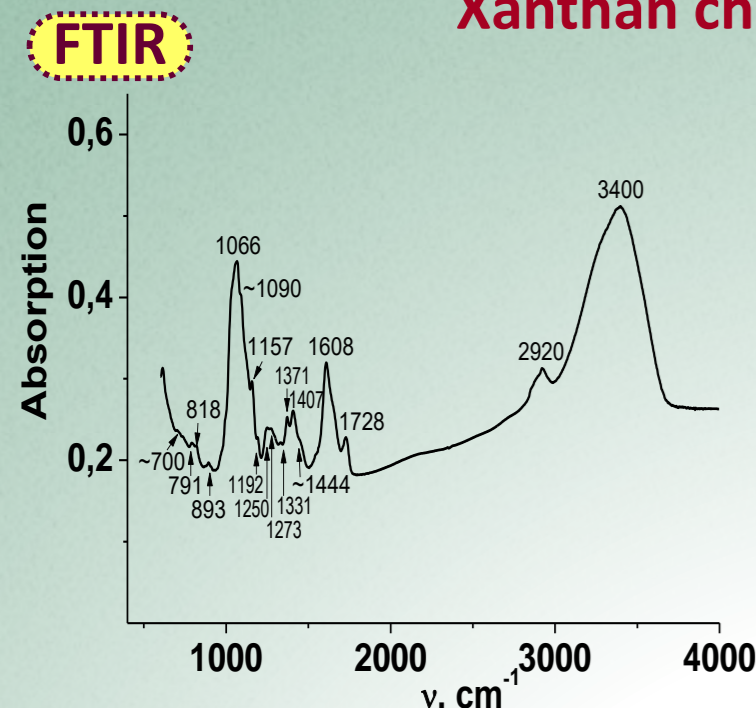
Heteropolysaccharide Xanthan and its properties

Generalized chemical structure of Xanthan



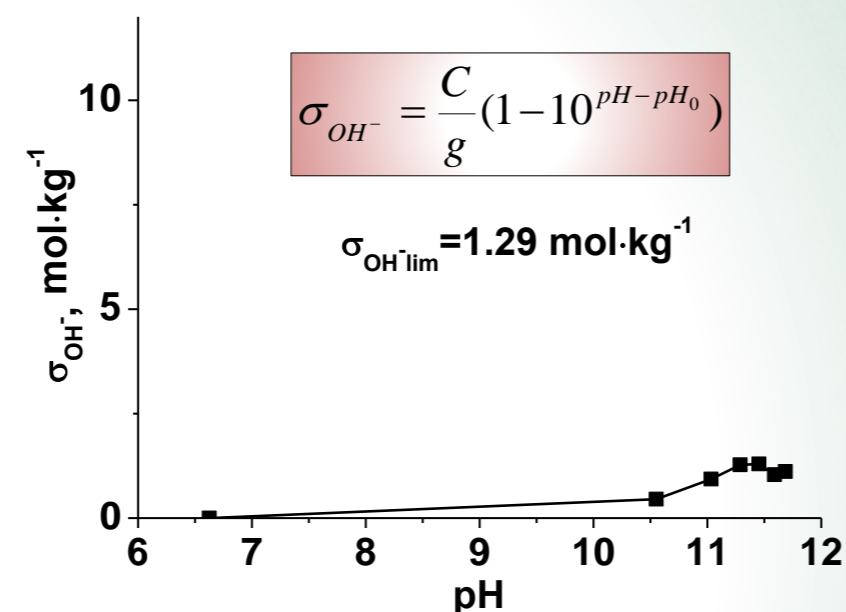
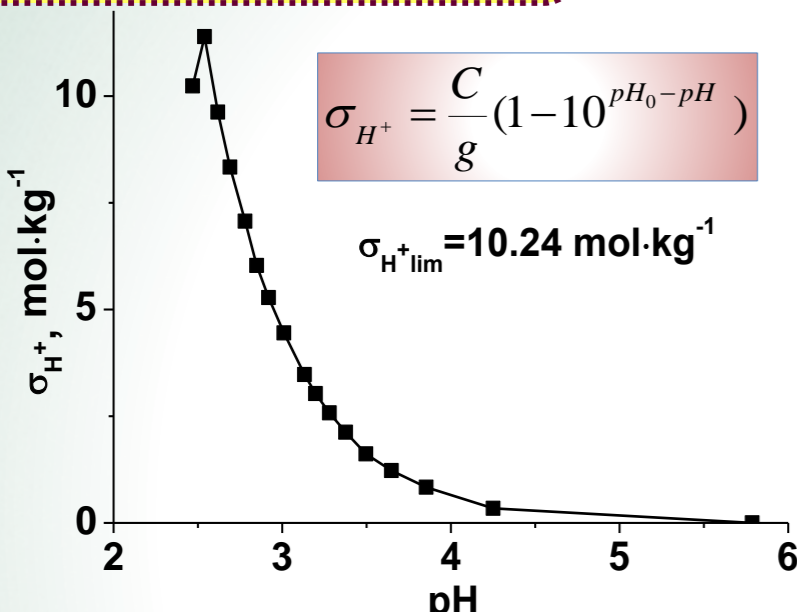
Xanthan contains a main chain of β -(1-4)-D-glucose units and trisaccharide side branches at the C3 atom of every second unit. These branches include D-glucuronic acid units (with a COOH group) between the D-mannose units. One link of D-mannose (with an acetyl group) is attached to the main chain, and the second one may contain a pyruvic acid moiety attached through a keto group.

Xanthan chemical structure confirmation



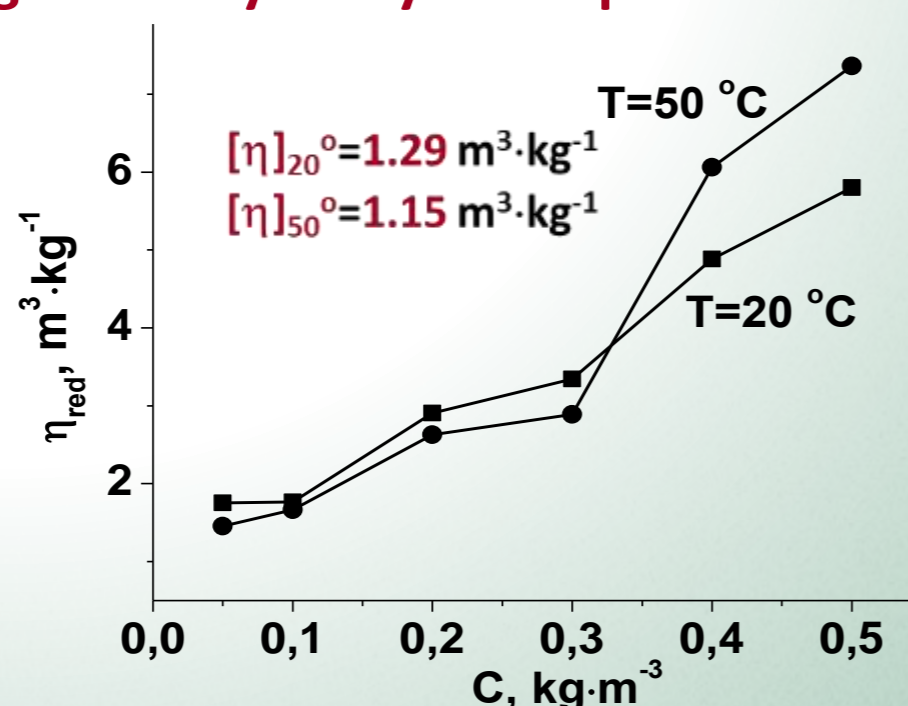
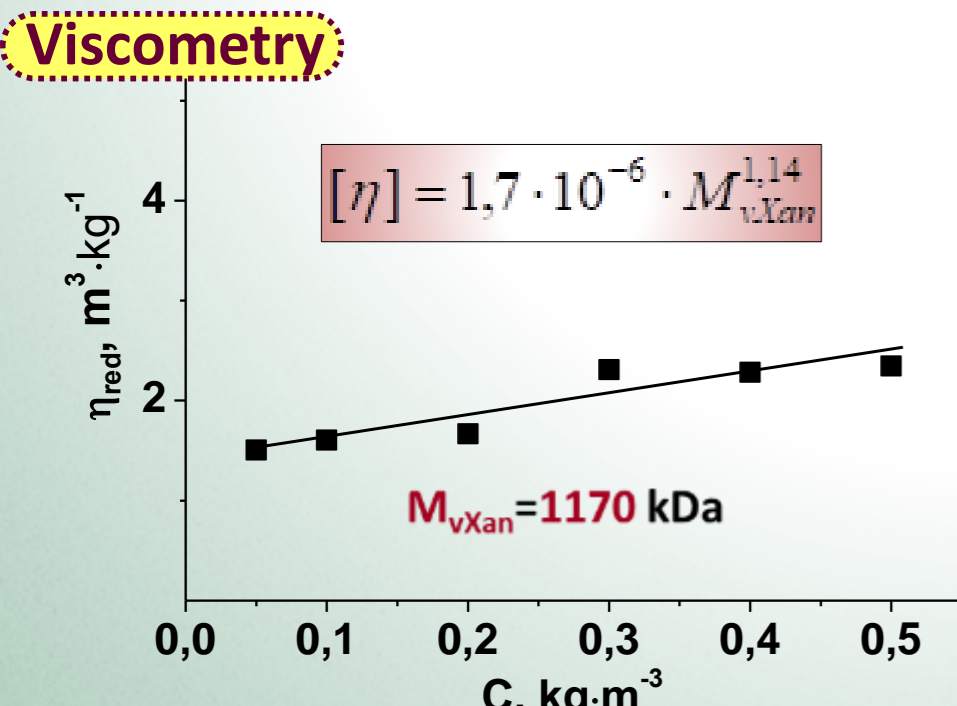
The FTIR spectrum contained an intense band of ν_{OH} vibrations of OH groups in Xanthan and adsorbed water molecules at 3400 cm^{-1} . OH-groups are also characterized by the in-plane and out-of-plane δ_{OH} vibrations at 1250 , 1275 cm^{-1} and $\sim 700\text{ cm}^{-1}$. The presence of a small number of COOH groups associated with OH groups was confirmed by the $\nu_{C=O}$ vibration band at 1728 cm^{-1} . The presence of COONa groups in the side branches was evidenced by the bands of ν_{COO^-} and ν_{C-O} vibrations of carboxylate ions at 1608 and 1407 cm^{-1} , as well as the band of ν_{Na-O} vibrations of Na⁺-ions at 818 cm^{-1} . Two intense bands at 1066 cm^{-1} and $\sim 1090\text{ cm}^{-1}$ corresponded to ν_{C-OH} and ν_{C-O-C} vibrations of the OH and C-O-C groups of Xanthan, and the bands at 1157 and 1192 cm^{-1} reflected $\nu_{C-O-Cas}$ vibrations of ether groups.

Potentiometric titration

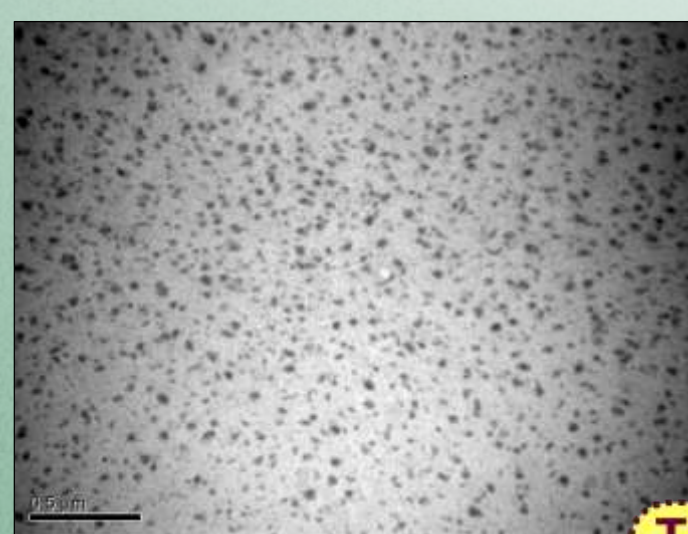


The number of COONa and COOH groups in Xanthan was 10.24 and 1.29 mol.kg^{-1} , respectively.

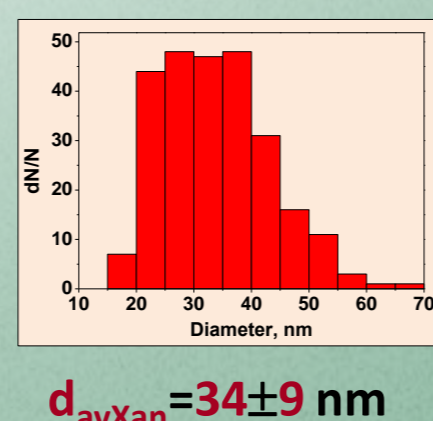
Determination of molecular weight and hydrodynamic parameters



Xanthan coils as physical nanogel particles in aqueous solutions



TEM

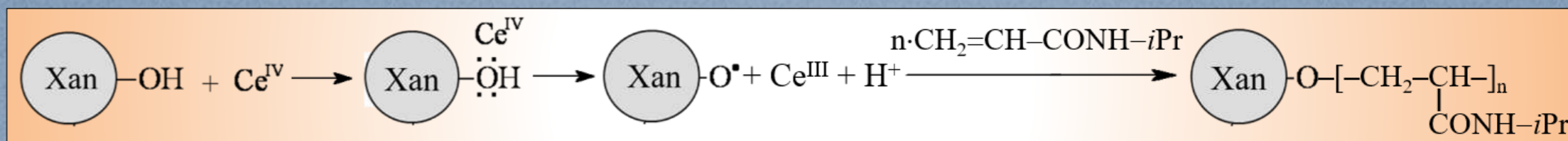


$d_{avXan} = 34 \pm 9\text{ nm}$

Xanthan coils are nanogel particles with a micelle-like structure. It can be assumed that their "core" is formed and stabilized mainly by hydrogen-bonded glucose units of the main chain. At the same time, their "corona" contains mainly side branches with negatively charged carboxylate and carboxyl groups.

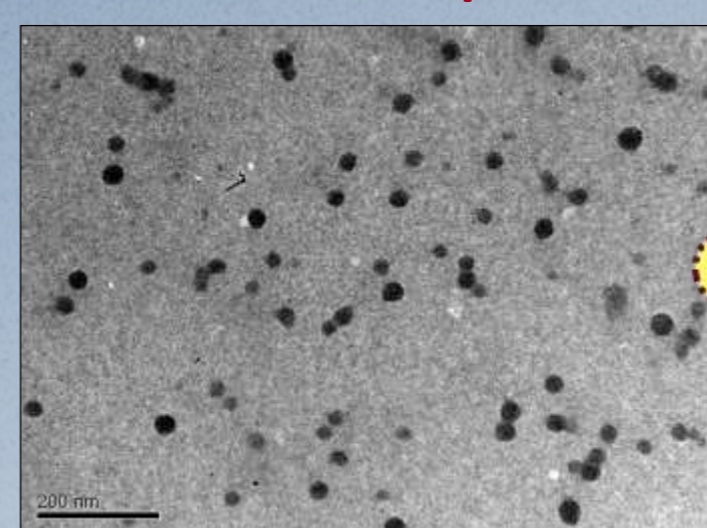
Synthesis and study of new polymer hybrids X-g-PIPAAm

Synthesis scheme and modeling of reaction mixtures

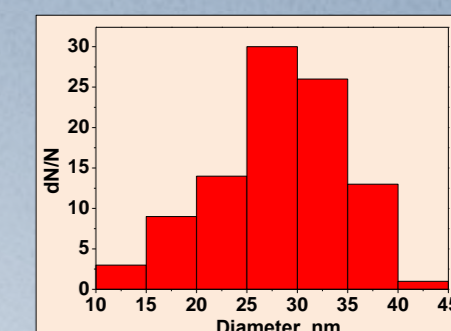
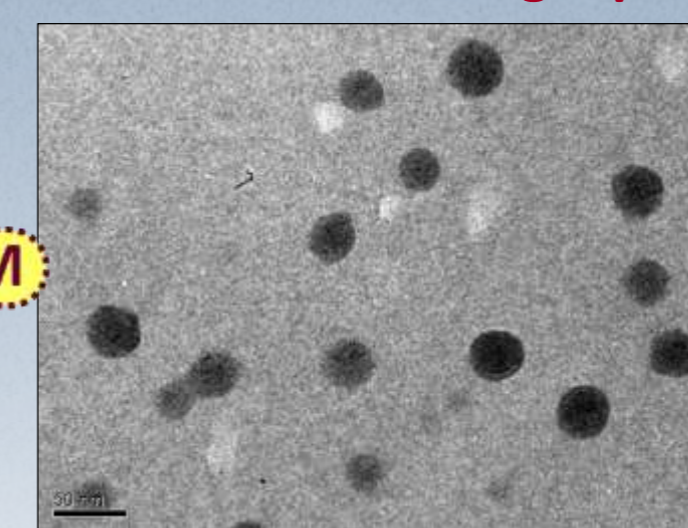


C_{Xan} =variable; C_{IPAAm} =const; C_{CeIV} =const

Complexes of CeIV with Xanthan nanogel particles

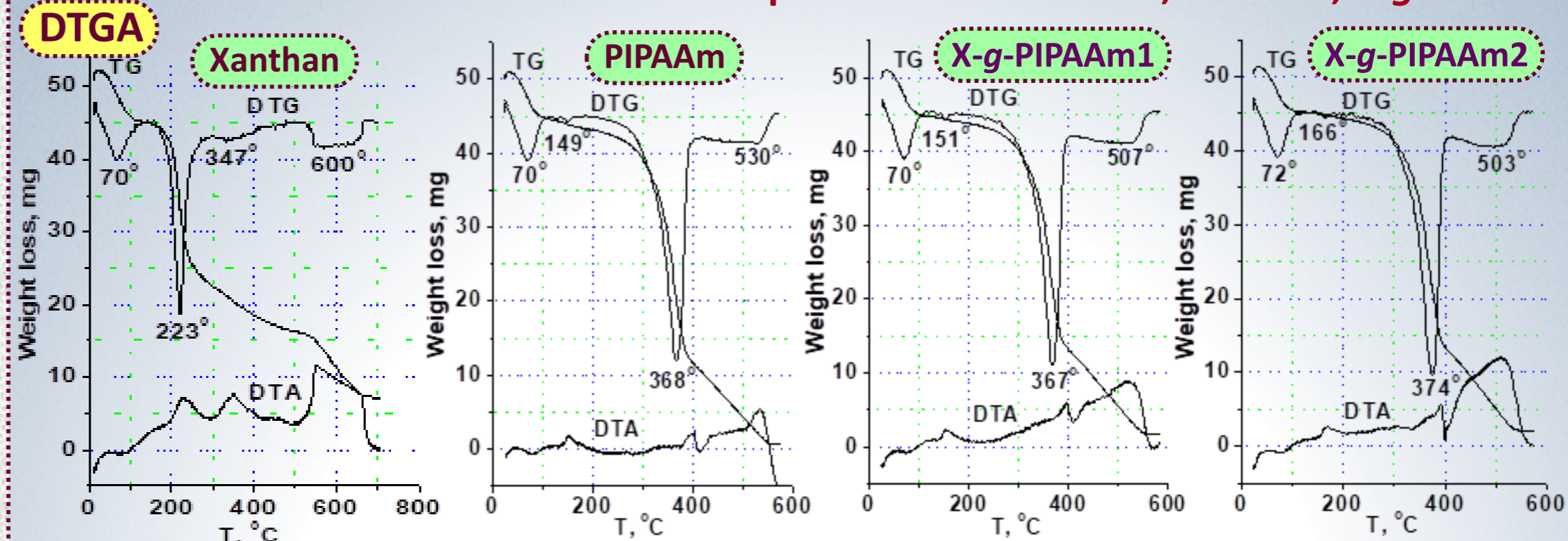


TEM



$d_{avCeIV/Xan} = 28 \pm 6\text{ nm}$

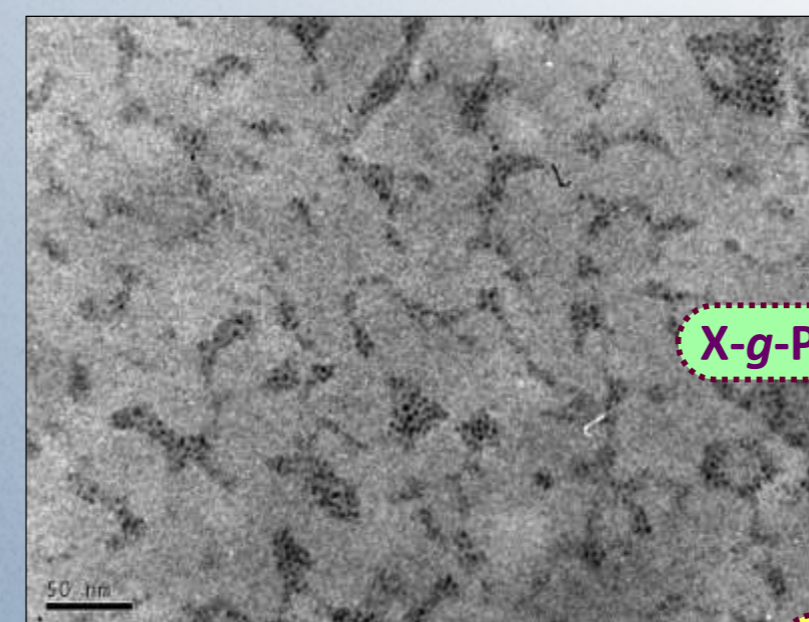
Water content and thermodestruction processes in Xanthan, PIPAAm, X-g-PIPAAm



Sample	H ₂ O ¹⁾ w %	Destruction stage	T _{beg} +T _{end} ²⁾ °C	ΔT ³⁾ °C	T _{max} ⁴⁾ °C	W ⁵⁾ w %	Residue w %	Thermal effect
Xanthan	10.1	I	157-255	98	223	39.7		Exo
		II	255-516	261	347	18.0		Exo
		III	516-700	184	600	16.9	7.0	Exo
PIPAAm	11.5	I	204-412	208	368	64.3		Endo, Exo
		II	412-566	154	530	20.3	1.6	Exo
X-g-PIPAAm1	10.9	I	208-413	205	367	63.0		Endo, Exo
		II	413-582	169	507	21.0	3.4	Exo
X-g-PIPAAm2	10.0	I	219-410	191	374	64.9		Exo, Exo
		II	410-569	159	503	21.3	4.1	Exo

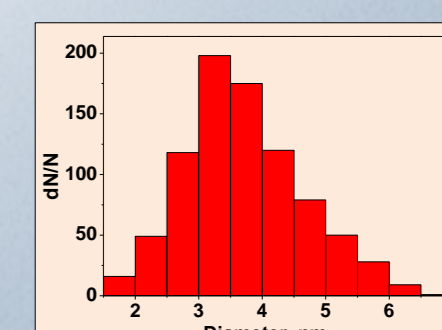
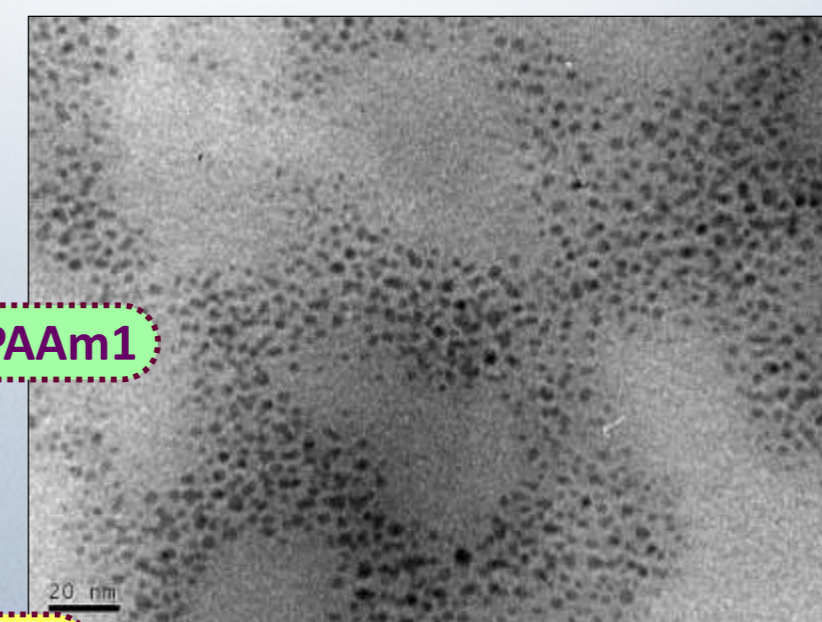
Increase in Xanthan content ↓

Morphology and size of hybrid nanoparticles

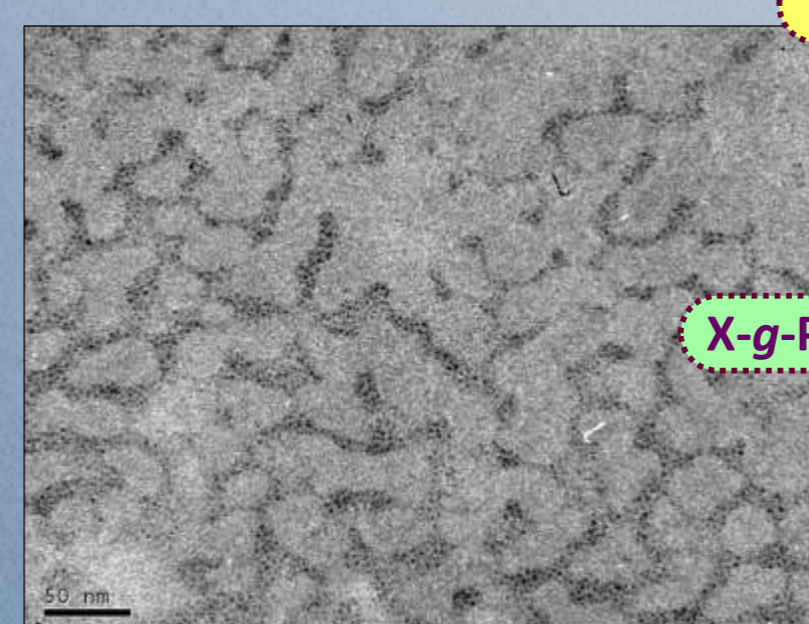


X-g-PIPAAm1

TEM

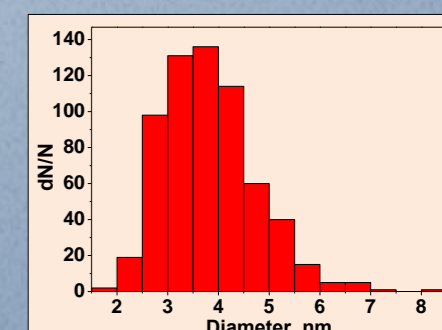
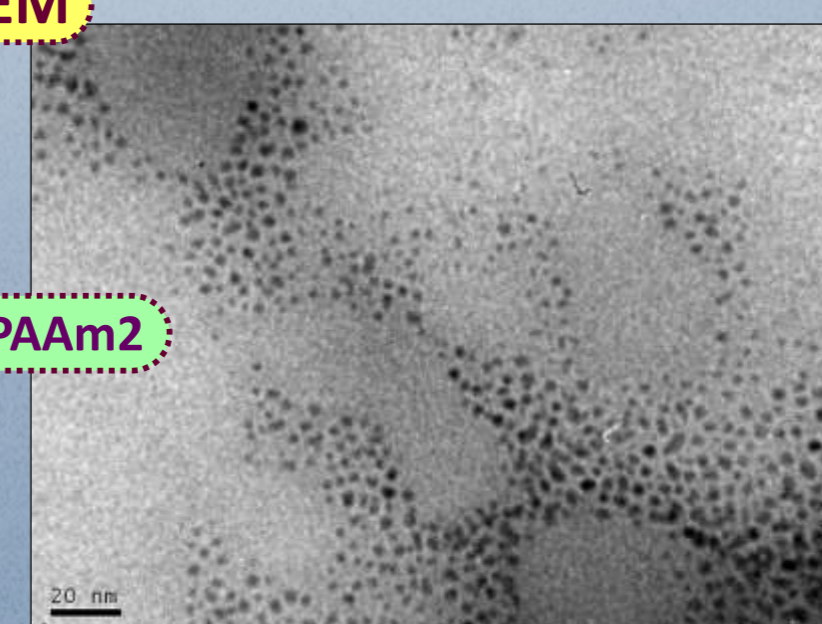


$d_{avHyb1} = 3.7 \pm 0.9\text{ nm}$



X-g-PIPAAm2

TEM



$d_{avHyb2} = 3.8 \pm 0.9\text{ nm}$

Conclusion

The chemical structure, molecular parameters, morphology, solution behavior, and coil size of a Xanthan sample produced by the bacteria *Xanthomonas campestris* were characterized using FTIR, viscometry, potentiometric titration, DTGA, and TEM. A series of X-g-PIPAAm hybrids with modeled constant length but increasing number of grafts was obtained by radical graft polymerization of IPAAm from the surface of Xanthan gel coils using the CeIV salt as the RedOx initiator. The interaction of the CeIV salt with Xanthan at the stage of initiation occurred only on the surface of polysaccharide coils. This did not cause the destruction of the structure of the nanoparticles, but only led to their compaction. As a result, new polymeric hybrids with a Xanthan nanogel "core" and a thermosensitive polymeric "corona" of PIPAAm were formed. The reprecipitated reaction products contained both components, which was confirmed by the data of elemental analysis, DTGA, and FTIR spectroscopy. According to TEM data, the resulting hybrid particles had a uniform structure, small size, and a narrow size distribution in an aqueous medium.